Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis and Lewis Acidity of Fluorinated Triaryl Borates

Mashael Alharbi,†[a,b] Yara van Ingen,†[a] Alberto Roldan[a], Tanja Kaehler[*a] and Rebecca L. Melen[*a]

[a] M. Alharbi, Y. van Ingen, Dr Alberto Roldan, Dr T. Kaehler, and Prof. R. L. Melen
Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, Cymru/Wales, United Kingdom.
E-mail: KaehlerT@cardiff.ac.uk, MelenR@cardiff.ac.uk

[b] Department of Chemistry, King Faisal University, College of Science, P.O. Box 400, Al-Ahsa 31982 Saudi Arabia

Table of Contents

1. Experimental

1.1 General experimental

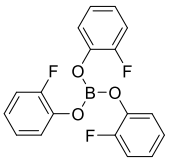
All reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBraun) was used for product recovery and sample preparation for analysis. All solvents (toluene, dichloromethane, pentane) were dried by employing a Grubbs-type column system (Innovative Technology) or a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance 500 spectrometers. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CDCl_3$ (7.26/77.16 ppm) as internal standard. Multinuclear NMR spectra were referenced to $CFCl_3$ (^{19}F) and $BF_3 \bullet Et_2O/CDCl_3$ (^{11}B).[1] The description of signals includes s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet, br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). ^{13}C NMR was measured as ^{1}H decoupled. Yields are given as isolated yields. Mass spectra were measured on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer. Ions were generated by the Atmospheric Solids, Analysis Probe (ASAP), Electrospray (ES) or Electron Ionisation (EI). The molecular ion peaks values are quoted as (M^+).

2. Product characterisation

2.1 General procedure A: The fluorinated triaryl borates were prepared using a modified literature procedure from Britovsek *et al*.[2] In a Schlenk flask, BCl_3 (1 M in hexane, 1 equiv.) was dissolved in 20 mL CH_2Cl_2 and cooled to -60 °C. To that, the corresponding phenol (3 equiv.), dissolved in 15 mL CH_2Cl_2, was added dropwise *via* cannula. The reaction was maintained at -60 °C for four hours while the forming gaseous HCl was trapped in an external cooling trap which was connected to the reaction flask. After letting the reaction warm to room temperature, the solvent was removed *in vacuo* and the crude product was left under dynamic vacuum for an additional 30 min to remove the excess BCl_3. The resulting crude product was purified *via* crystallisation.

2.2 Synthesis and spectral characterisation of the borate esters

Synthesis of tris(2-fluorophenyl)borate (**1**)

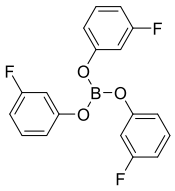


Synthesised in accordance with *General Procedure A* using 2-fluorophenol (1.5 g, 13.5 mmol), BCl_3 (4.5 mL, 4.5 mmol, 1 M in hexane) in CH_2Cl_2 to afford **1**. The crude reaction mixture was purified by crystallising the compound from a concentrated solution of pentane at -35 °C and washing the obtained crystalline solid with cold pentane. The desired compound **1** was obtained as a colourless solid. Yield: 1.15 g, 3.34 mmol, 74 %. Single crystals suitable for X-ray diffraction analysis were grown from a saturated solution of **1** in CH_2Cl_2 at -35 °C.

The values are in consistent with previously reported data.[3]

^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.18–7.22 (m, 3H), 7.01–7.16 ppm (m, 9H); **^{11}B NMR** (128.0 MHz, $CDCl_3$) δ: 16.5 ppm (br. s); **^{19}F NMR** (376.5 MHz, $CDCl_3$) δ: -132.28 ppm (s, 3F); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 153.7 (d, $J_{C–F}$ = 246.0 Hz), 140.7 (d, $J_{C–F}$ = 11.5 Hz), 124.8 (d, $J_{C–F}$ = 6.5 Hz), 124.5 (d, $J_{C–F}$ = 3.7 Hz), 122.5, 116.6 ppm (d, $J_{C–F}$ = 18.5 Hz); **HRMS** (CI) $[M^+]$ $[C_{18}H_{12}O_3F_3B]^+$: calculated 344.0826, found 344.0825; **Elemental Analysis**: Found: C, 62.63; H, 3.31; N, 0%, Calcd for $C_{18}H_{12}BF_3O_3$: C, 62.83; H, 3.52; N, 0%.

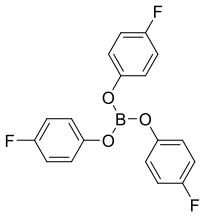
Synthesis of tris(3-fluorophenyl)borate (**2**)



Synthesised in accordance with *General Procedure A* using 3-fluorophenol (1.5 g, 13.5 mmol), BCl_3 (4.5 mL, 4.5 mmol, 1 M in hexane) in CH_2Cl_2 to afford **2**. The desired compound **2** was obtained as a colourless oil without any further purification. Yield: 1.40 g, 4.07 mmol, 90 %.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.24–7.29 (m, 3H), 6.78–7.94 ppm (m, 9H); **^{11}B NMR** (128.0 MHz, $CDCl_3$) δ:15.9 ppm (br. s); **^{19}F NMR** (376.5 MHz, $CDCl_3$) δ: -111.53 ppm (s, 3F); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 162.1 (d, $J_{C–F}$ = 244.6 Hz), 152.5 (d, $J_{C–F}$ = 11.3 Hz), 129.1 (d, $J_{C–F}$ = 9.2 Hz), 114.9 (d, $J_{C–F}$ = 3.2 Hz), 109.9 (d, $J_{C–F}$ = 21.1 Hz), 107.1 ppm (d, $J_{C–F}$ = 24.2 Hz); **HRMS** (CI) $[M^+]$ $[C_{18}H_{12}O_3F_3B]^+$: calculated 344.0826, found 344.0823; **Elemental Analysis**: Found: C, 61.23; H, 3.63; N, 0%, Calcd for $C_{18}H_{12}BF_3O_3$: C, 62.83; H, 3.52; N, 0%.

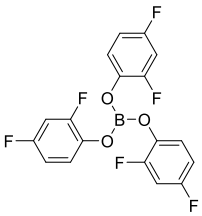
Synthesis of tris(4-fluorophenyl)borate (**3**)



Synthesised in accordance with *General Procedure A* using 4-fluorophenol (1.5 g, 13.5 mmol), BCl_3 (4.5 mL, 4.5 mmol, 1 M in hexane) in CH_2Cl_2 to afford **3**. The crude reaction mixture was purified by crystallising the compound from a concentrated solution of pentane at -35 °C and washing the obtained crystalline solid with cold pentane. The desired compound **3** was obtained as a colourless solid. Yield: 1.37 g, 3.98 mmol, 88 %.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 6.94–7.09 ppm (m, 12H); **^{11}B NMR** (128.0 MHz, $CDCl_3$) δ:16.3 ppm (br. s); **^{19}F NMR** (376.5 MHz, $CDCl_3$) δ: -120.06 ppm (s, 3F); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 159.1 (d, $J_{C–F}$ = 241.6 Hz), 148.8 (d, $J_{C–F}$ = 2.8 Hz), 121.4 (d, $J_{C–F}$ = 8.3 Hz), 116.0 ppm (d, $J_{C–F}$ = 23.3 Hz); **HRMS** (CI) $[M^+]$ $[C_{18}H_{12}O_3F_3B]^+$: calculated 344.0826, found 344.0824; **Elemental Analysis**: Found: C, 62.83; H, 3.68; N, 0%, Calcd for $C_{18}H_{12}BF_3O_3$: C, 62.83; H, 3.52; N, 0%.

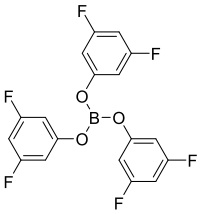
Synthesis of tris(2,4-difluorophenyl)borate (**4**)



Synthesised in accordance with *General Procedure A* using 2,4-difluorophenol (1.5 g, 13.5 mmol), BCl_3 (4.5 mL, 4.5 mmol, 1 M in hexane) in CH_2Cl_2 to afford **4**. The crude reaction mixture was purified by crystallising the compound from a concentrated solution of pentane at -35 °C and washing the obtained crystalline solid with cold pentane. The desired compound **4** was obtained as a colourless solid. Yield: 1.34 g, 3.37 mmol, 75 %.

^{1}H NMR (400.1 MHz, C_2D_6) δ: 6.77–6.84 (m, 3H), 6.53–6.59 (m, 3H), 6.38–6.44 ppm (m, 3H); **^{11}B NMR** (128.4 MHz, $CDCl_3$) δ: 16.7 ppm (br. s); **^{19}F NMR** (376.5 MHz, $CDCl_3$) δ: -115.28 (s, 3F), -127.63 ppm (s, 3F); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 158.8 (dd, $J_{C–F}$ = 245.0, 10.7 Hz), 153.3 (dd, $J_{C–F}$ = 249.6, 10.7 Hz), 136.9 (dd, $J_{C–F}$ = 12.0, 3.9 Hz), 122.6 (d, $J_{C–F}$ = 9.6 Hz), 111.1 (d, $J_{C–F}$ = 23.4 Hz), 105.0 ppm (dd, $J_{C–F}$ = 22.7, 22.4 Hz); **HRMS** (CI) [M^+] $[C_{18}H_9O_3F_6B]^+$: calculated 398.0544, found 398.0542.

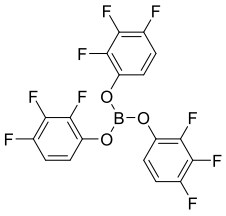
Synthesis of tris(3,5-difluorophenyl)borate (**5**)



Synthesised in accordance with *General Procedure A* using 3,5-difluorophenol (1.8 g, 13.5 mmol), BCl_3 (4.5 mL, 4.5 mmol, 1 M in hexane) in CH_2Cl_2 to afford **5**. The crude reaction mixture was purified by crystallising the compound from a concentrated solution of pentane at -35 °C and washing the obtained crystalline solid with cold pentane. The desired compound **5** was obtained as a colourless solid. Yield: 1.63 g, 4.09 mmol, 91 %.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 6.60–6.72 ppm (m, 9H); **^{11}B NMR** (128.4 MHz, $CDCl_3$) δ: 15.6 ppm (br. s); **^{19}F NMR** (376.5 MHz, $CDCl_3$) δ: -108.67 ppm (s, 6F); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 163.3 (dd, $J_{C–F}$ = 246.0, 15.2 Hz), 153.7 (t, $J_{C–F}$ = 14.1, 14.1 Hz), 104.3–104.6 (m), 100.3 ppm (t, $J_{C–F}$ = 25.5, 25.5 Hz); **HRMS** (CI) [ligand] $[C_6H_4OF_2]^+$: calculated 130.0225, found 130.0224.

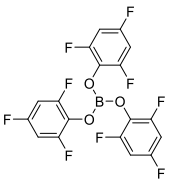
Synthesis of tris(2,3,4-trifluorophenyl)borate (**6**)



Synthesised in accordance with *General Procedure A* using 2,3,4-trifluorophenol (2.0 g, 13.5 mmol), BCl_3 (4.5 mL, 4.50 mmol, 1 M in hexane) in CH_2Cl_2 to afford **6**. The crude reaction mixture was purified by crystallising the compound from a concentrated solution of pentane at -35 ˚C and washing the obtained crystalline solid with cold pentane. The desired compound **6** was obtained as a pale pink solid. Yield: 1.82 g, 4.03 mmol, 89 %.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 6.91–6.95 ppm (m, 6H); **^{11}B NMR** (128.4 MHz, $CDCl_3$) δ 16.5 ppm (br. s); **^{19}F NMR** (376.5 MHz, $CDCl_3$) δ: -138.94 (d, 3F, $J_{C–F}$ = 20.2 Hz), -150.27 (d, 3F, $J_{C–F}$ = 18.8 Hz), -157.18 ppm (t, 3F, $J_{C–F}$ = 20.0 Hz); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 148.1 (dd, $J_{C–F}$ = 247.8, 10.1 Hz), 143.5 (ddd, $J_{C–F}$ = 251.3, 11.6, 3.8 Hz), 140.8 (ddd, $J_{C–F}$ = 251.8, 11.6, 10.1 Hz), 137.4 (dd, $J_{C–F}$ = 9.5, 3.6 Hz), 115.6 (dd, $J_{C–F}$ = 7.6, 3.9 Hz), 111.1 ppm (dd, $J_{C–F}$ = 18.7, 3.5 Hz); **HRMS** (CI) [ligand] $[C_6H_3OF_3]^+$: calculated 184.0131, found 148.0129; **Elemental Analysis**. Found: C, 46.71; H, 1.37; N, 0%, Calcd for $C_{18}H_6O_3F_9B$: C, 47.83; H, 1.34; N, 0%.

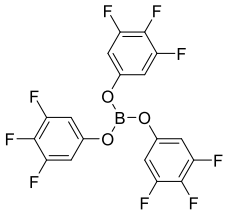
Synthesis of tris(2,4,6-trifluorophenyl)borate (**7**)



Synthesised in accordance with *General Procedure A* using 2,4,6-trifluorophenol (0.30 g, 2.0 mmol) in 10 mL CH_2Cl_2, BCl_3 (0.68 mL, 0.68 mmol, 1M in hexane) in 10 mL CH_2Cl_2 to afford **7**. The crude reaction mixture was purified by crystallising the compound from a concentrated solution of pentane at -35 ˚C and washing the obtained crystalline solid with cold pentane. The desired compound **7** was obtained as a colourless solid. Yield: 0.26 g, 0.57 mmol, 85%. Single crystals suitable for X-ray diffraction analysis were grown from a saturated solution of **7** in CH_2Cl_2 at -35 ˚C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96–6.90 ppm (m, 6H); **^{11}B NMR** (128 MHz, $CDCl_3$) δ: 17.7 ppm (br. s); **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -119.47 (s, 1F), -132.73 ppm (s, 2F); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 156.2 (t, $J_{C–F}$ = 13.8 Hz), 153.6 (t, $J_{C–F}$ = 13.9 Hz), 152.7 (dd, $J_{C–F}$ = 14.6, 7.3 Hz), 150.2 (dd, $J_{C–F}$ = 14.5, 7.7 Hz), 130.0-129.6 (m), 100.3 (dd, $J_{C–F}$ = 26.9, 8.6 Hz), 100.3 ppm (t, $J_{C–F}$ = 26.8 Hz); **HRMS** (CI) $[M^+]$ $[C_{18}H_6O_3F_9B]^+$: calculated 451.0297, found 451.0298.

Synthesis of tris(3,4,5-trifluorophenyl)borate (**8**)



Synthesised in accordance with *General Procedure A* using 3,4,5-trifluorophenol (2.0 g, 13.5 mmol), BCl_3 (4.5 mL, 4.5 mmol, 1 M in hexane) in CH_2Cl_2 to afford **8**. The crude reaction mixture was purified by crystallising the compound from a concentrated solution of CH_2Cl_2 at -35 °C and washing the obtained crystalline solid with cold pentane. The desired compound **8** was obtained as a colourless solid. Yield: 1.7 g, 3.8 mmol, 84%. Single crystals suitable for X-ray diffraction analysis were grown from a saturated solution of **8** in CH_2Cl_2 at -35 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 6.71–6.85 ppm (m, 6H); **^{11}B NMR** (128.0 MHz, $CDCl_3$) δ: 15.7 ppm (br. s); **^{19}F NMR** (376.5 MHz, $CDCl_3$) δ: -132.61 (d, 6F, $J_{F–F}$ = 21.1 Hz), -165.44 ppm (t, 3F, $J_{F–F}$ = 21.1 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 151.3 (ddd, $J_{C–F}$= 251.2, 15.2, 5.5 Hz), 147.0 (td, $J_{C–F}$ = 13.0, 3.9 Hz), 137.4 (dt, $J_{C–F}$ = 248.6, 15.2 Hz), 105.4 ppm (dd, $J_{C–F}$ = 23.1 , 6.3 Hz); **HRMS** (CI) $[M^+]$ $[C_{18}H_6O_3F_9B]^+$: calculated 451.0297, found 451.0298; **Elemental Analysis**. Found: C, 47.73; H, 1.23; N, 0%, Calcd for $C_{18}H_6O_3F_9B$: C, 47.83; H, 1.34; N, 0%.

3. NMR spectra of the fluorinated triaryl borates

Figure S1: **^{1}H NMR** (400.1 MHz, $CDCl_3$) spectrum of tris(2-fluorophenyl)borate (**1**).

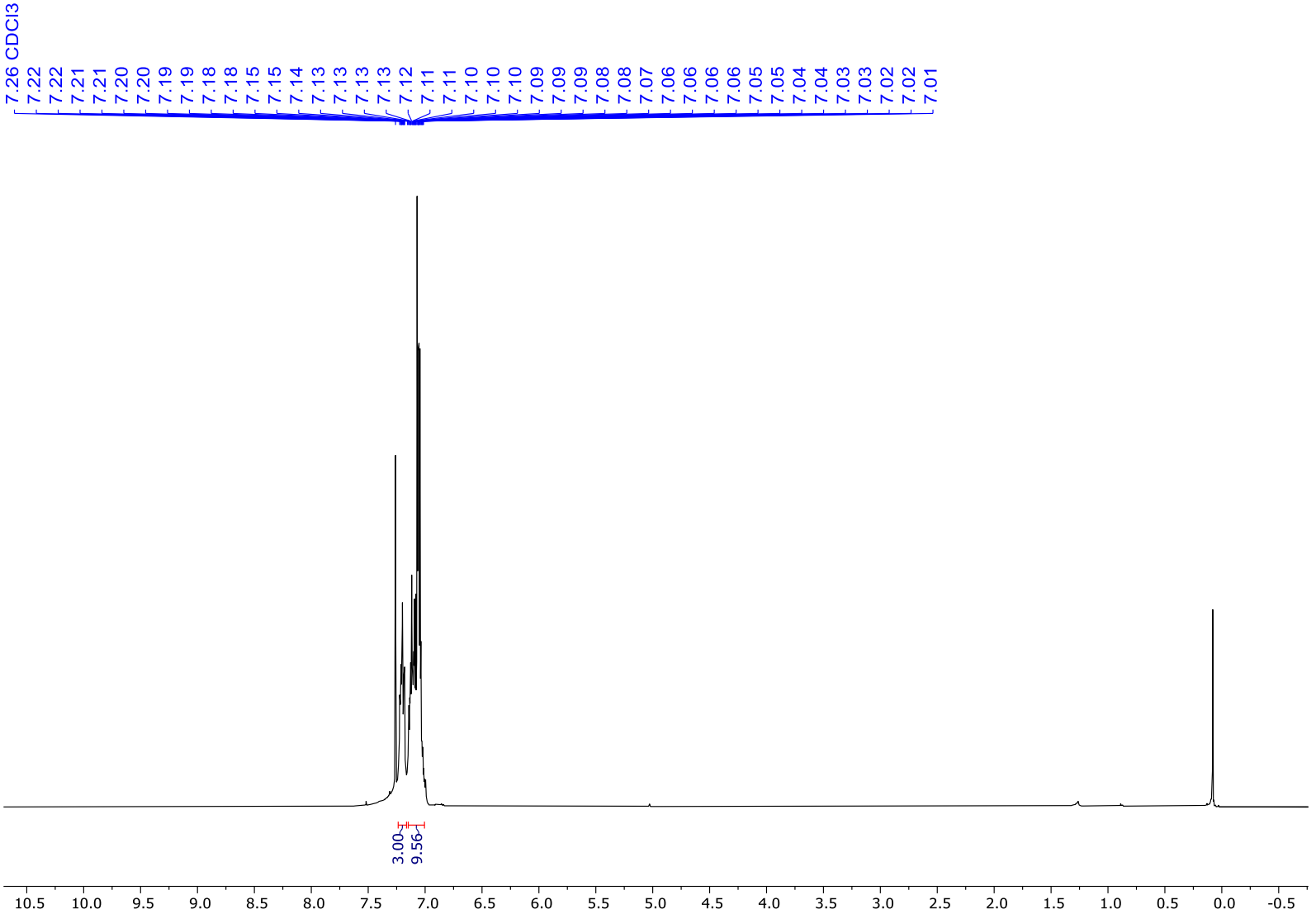


Figure S2: **^{11}B NMR** (128.4 MHz, $CDCl_3$) spectrum of tris(2-fluorophenyl)borate (**1**).

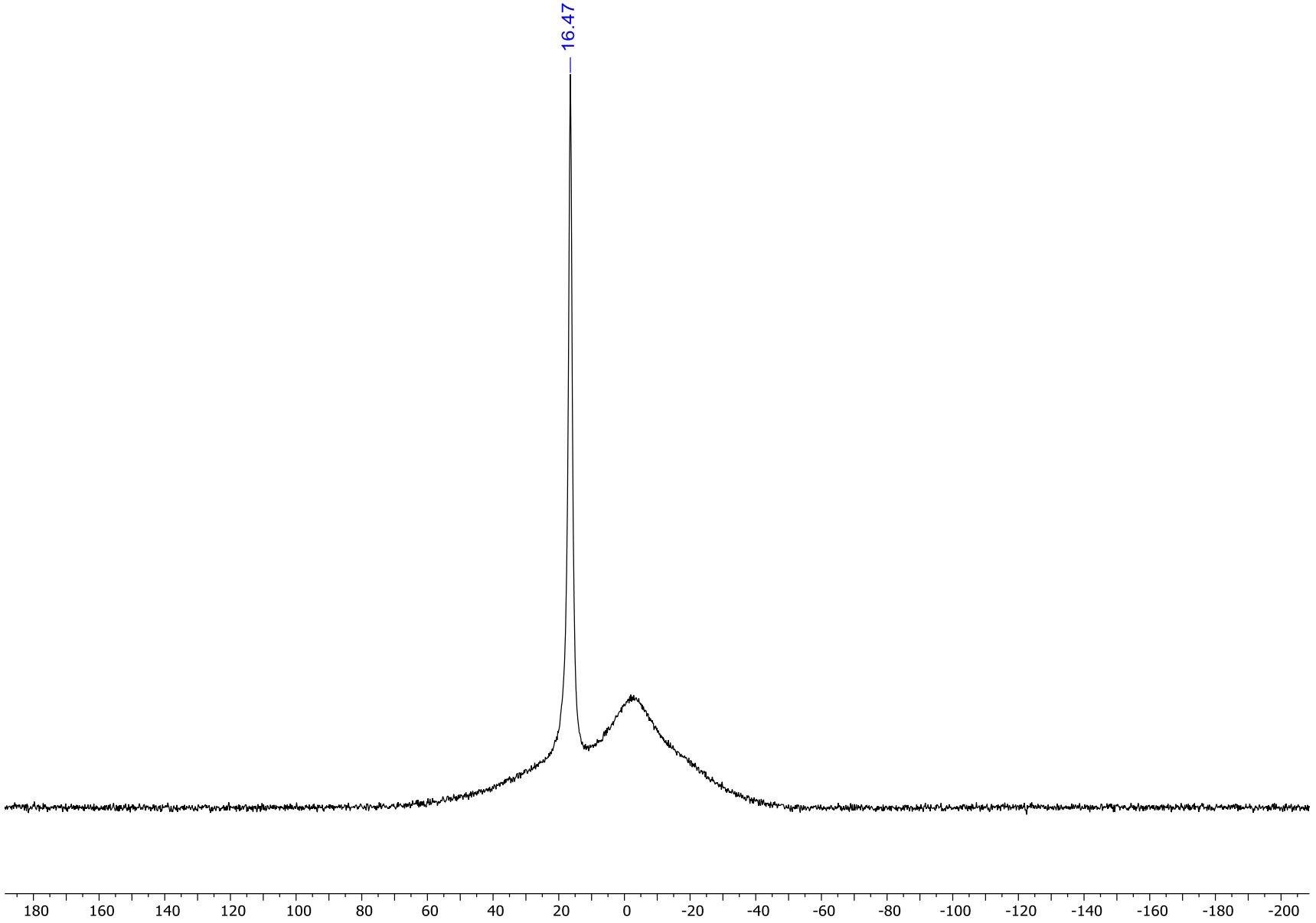


Figure S3: **^{19}F NMR** (376.5 MHz, $CDCl_3$) spectrum of tris(2-fluorophenyl)borate (**1**).

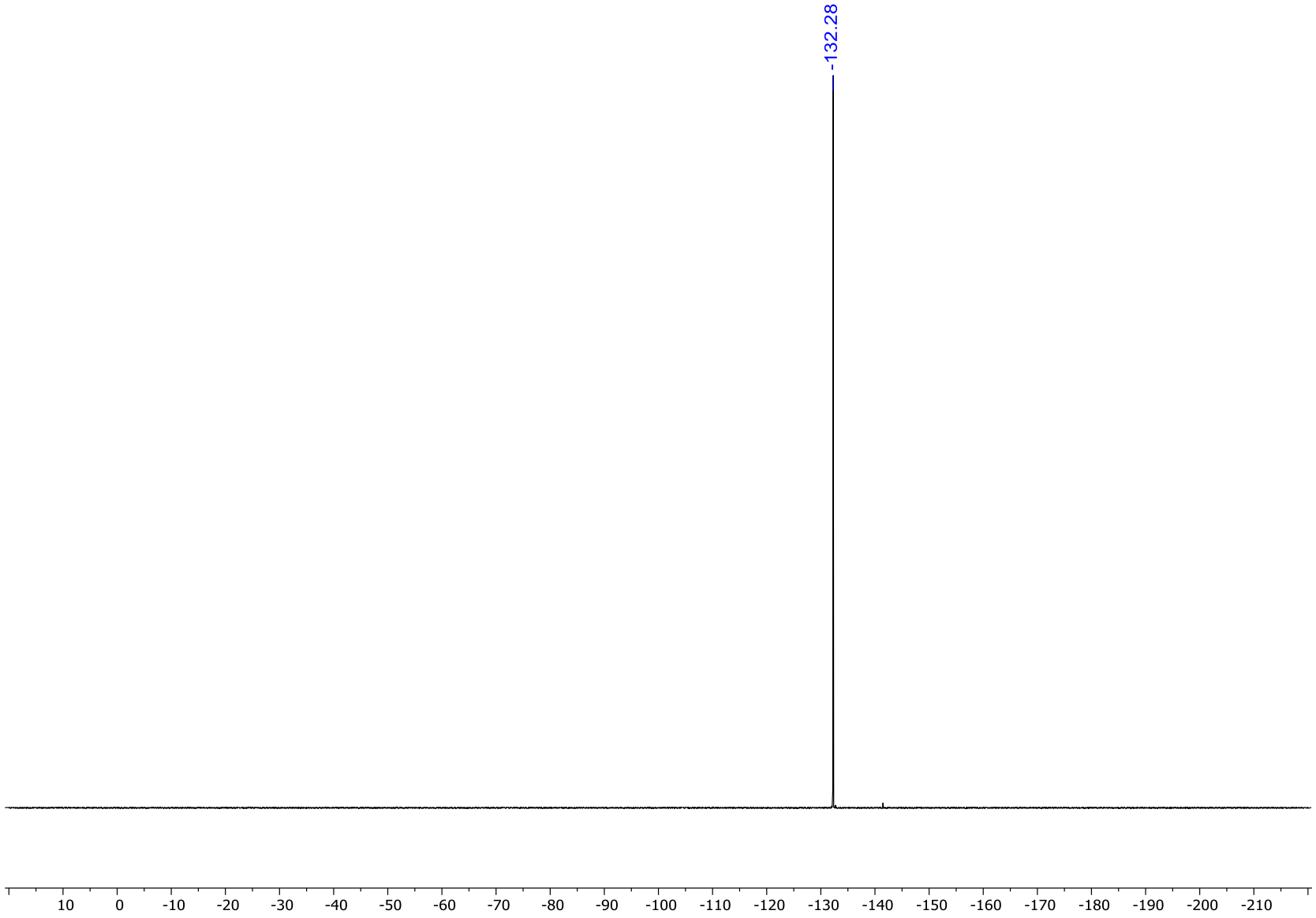


Figure S4: **^{13}C NMR** (125.8 MHz, $CDCl_3$) spectrum of tris(2-fluorophenyl)borate (**1**).

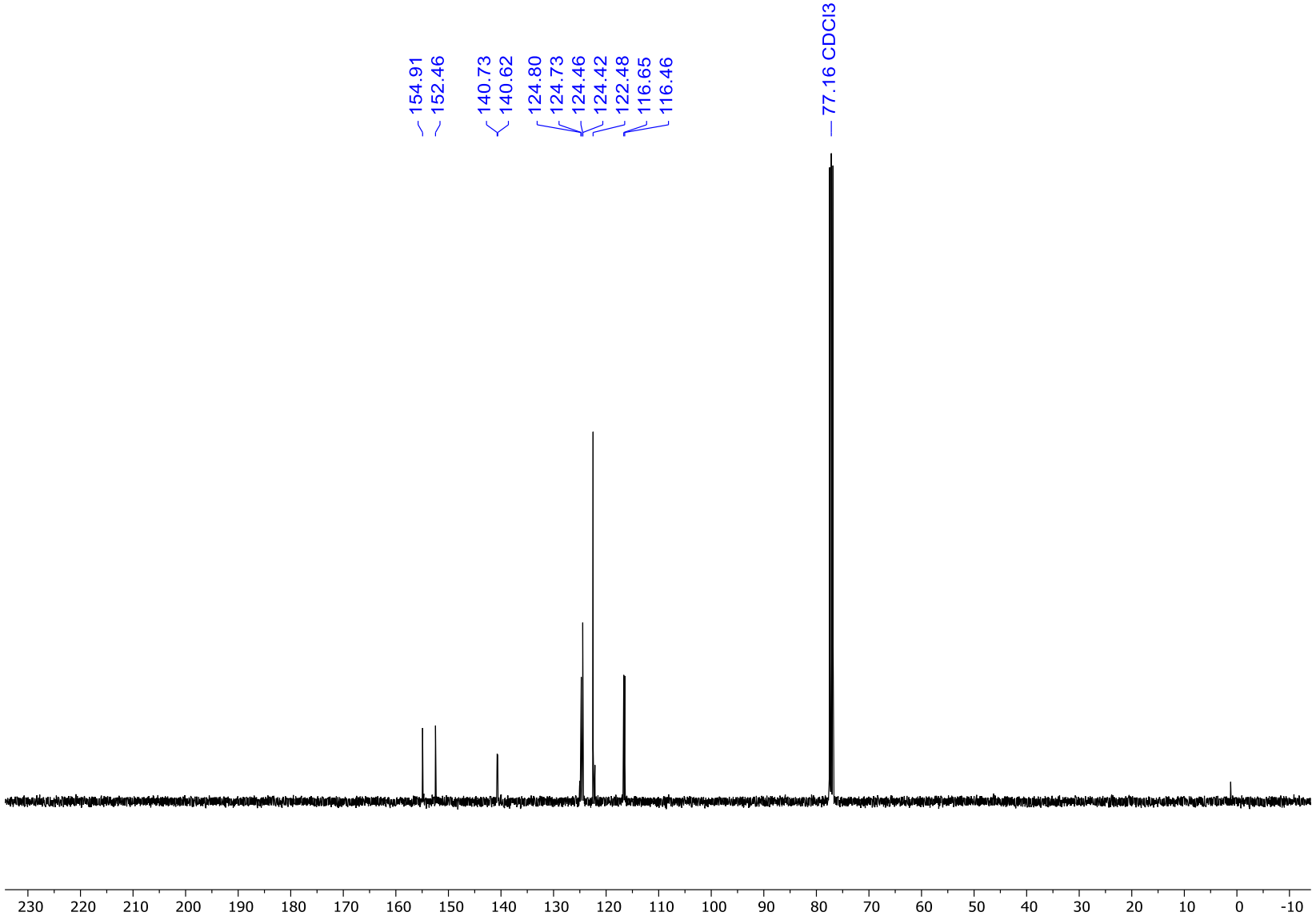


Figure S5: **^{1}H NMR** (400.1 MHz, $CDCl_3$) spectrum of tris(3-fluorophenyl)borate (**2**).

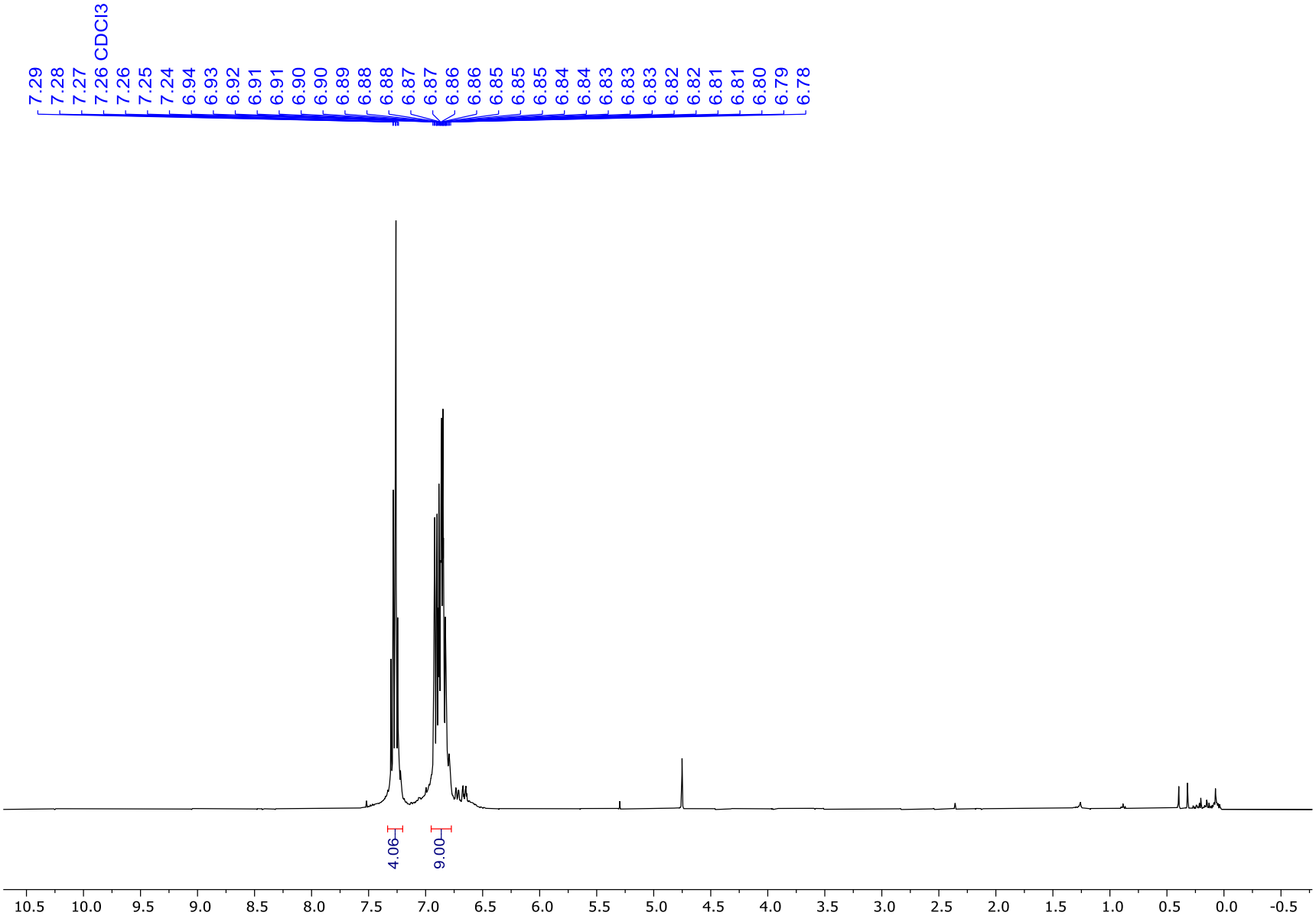


Figure S6: **^{11}B NMR** (128.4 MHz, $CDCl_3$) spectrum of tris(3-fluorophenyl)borate (**2**).

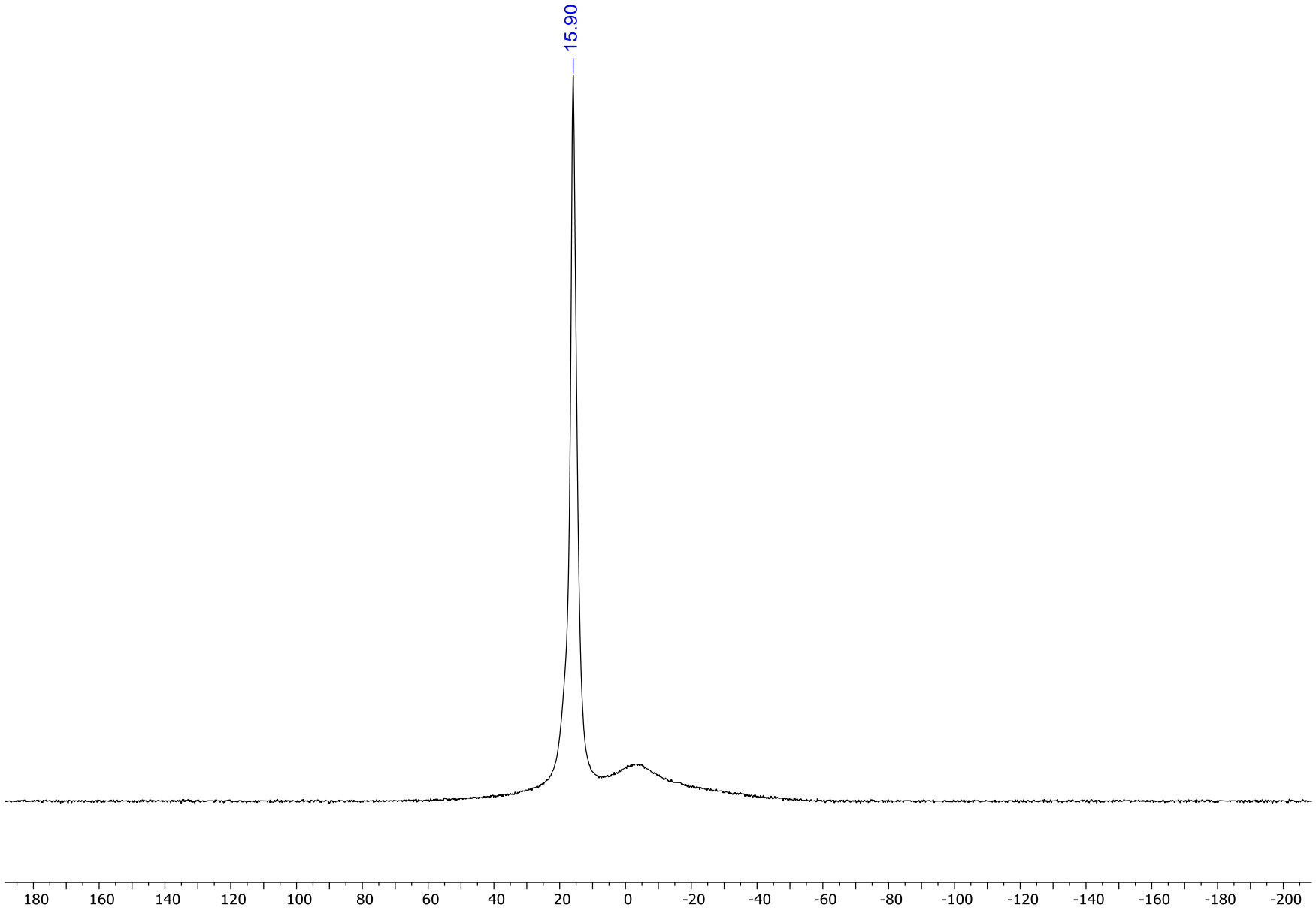


Figure S7: **^{19}F NMR** (376.5 MHz, $CDCl_3$) spectrum of tris(3-fluorophenyl)borate (**2**).

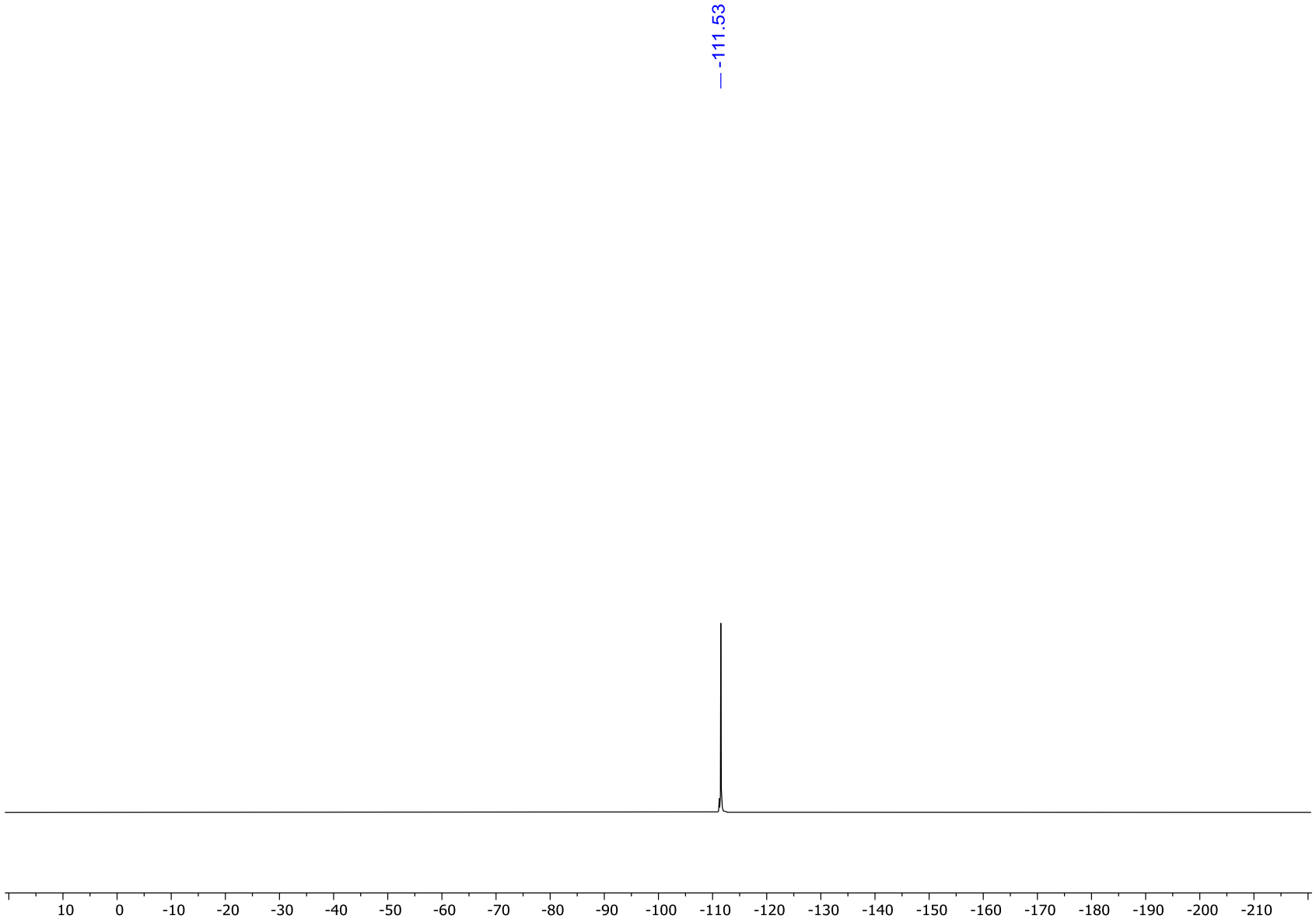


Figure S8: **^{13}C NMR** (100.6 MHz, $CDCl_3$) spectrum of tris(3-fluorophenyl)borate (**2**).

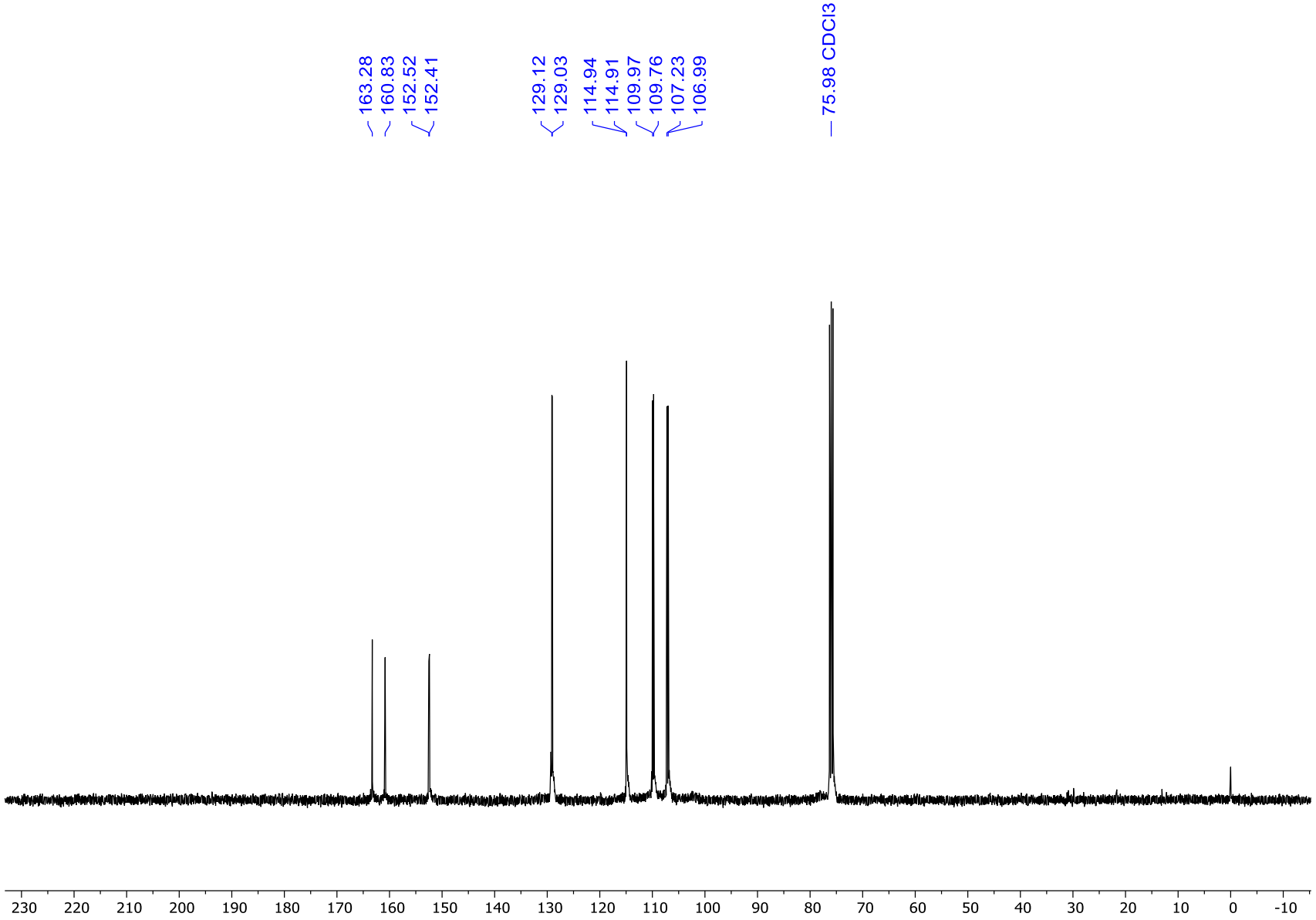


Figure S9: **^{1}H NMR** (400.1 MHz, $CDCl_3$) spectrum of tris(4-fluorophenyl)borate (**3**).

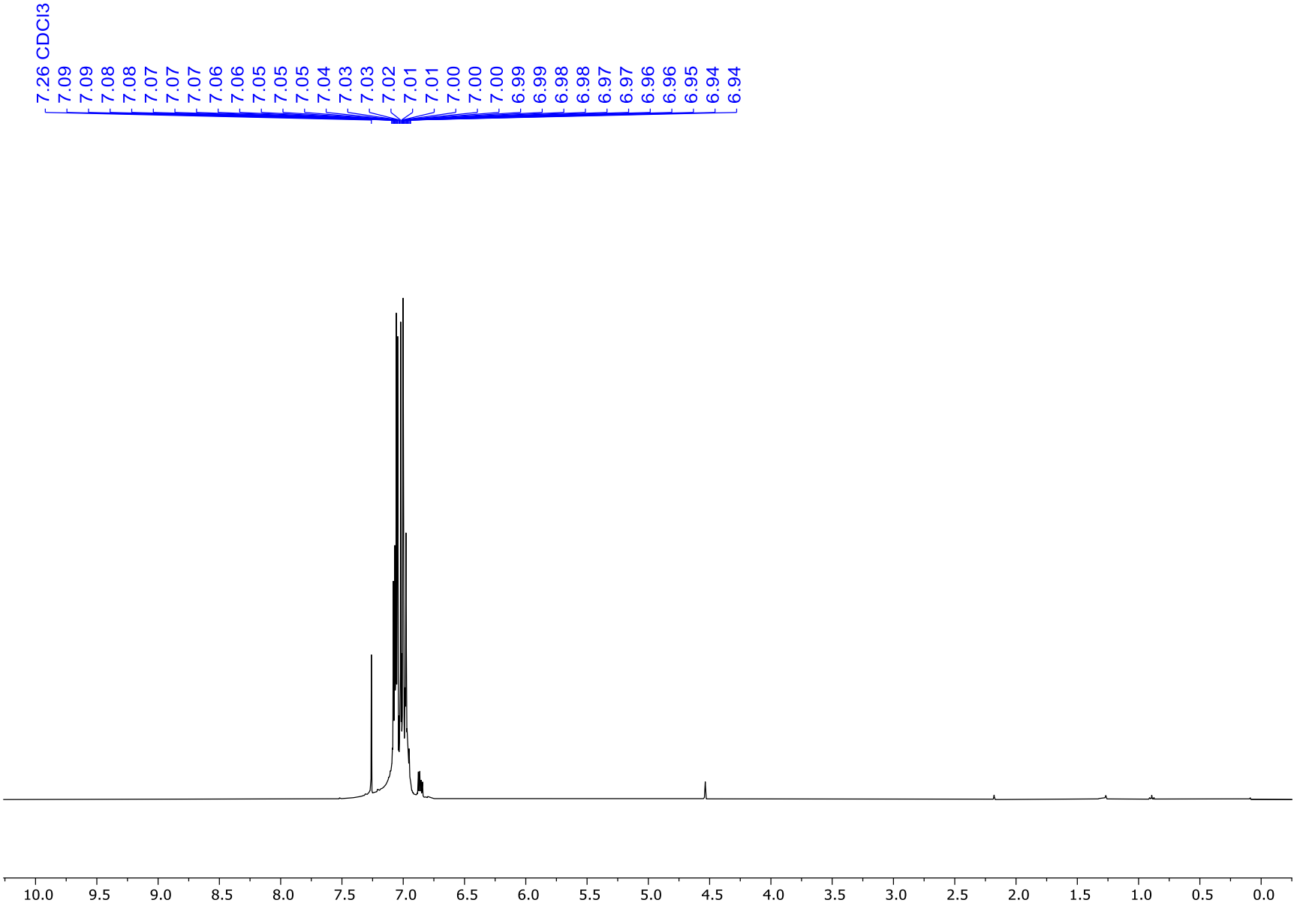


Figure S10: **^{11}B NMR** (128.4 MHz, $CDCl_3$) spectrum of tris(4-fluorophenyl)borate (**3**).

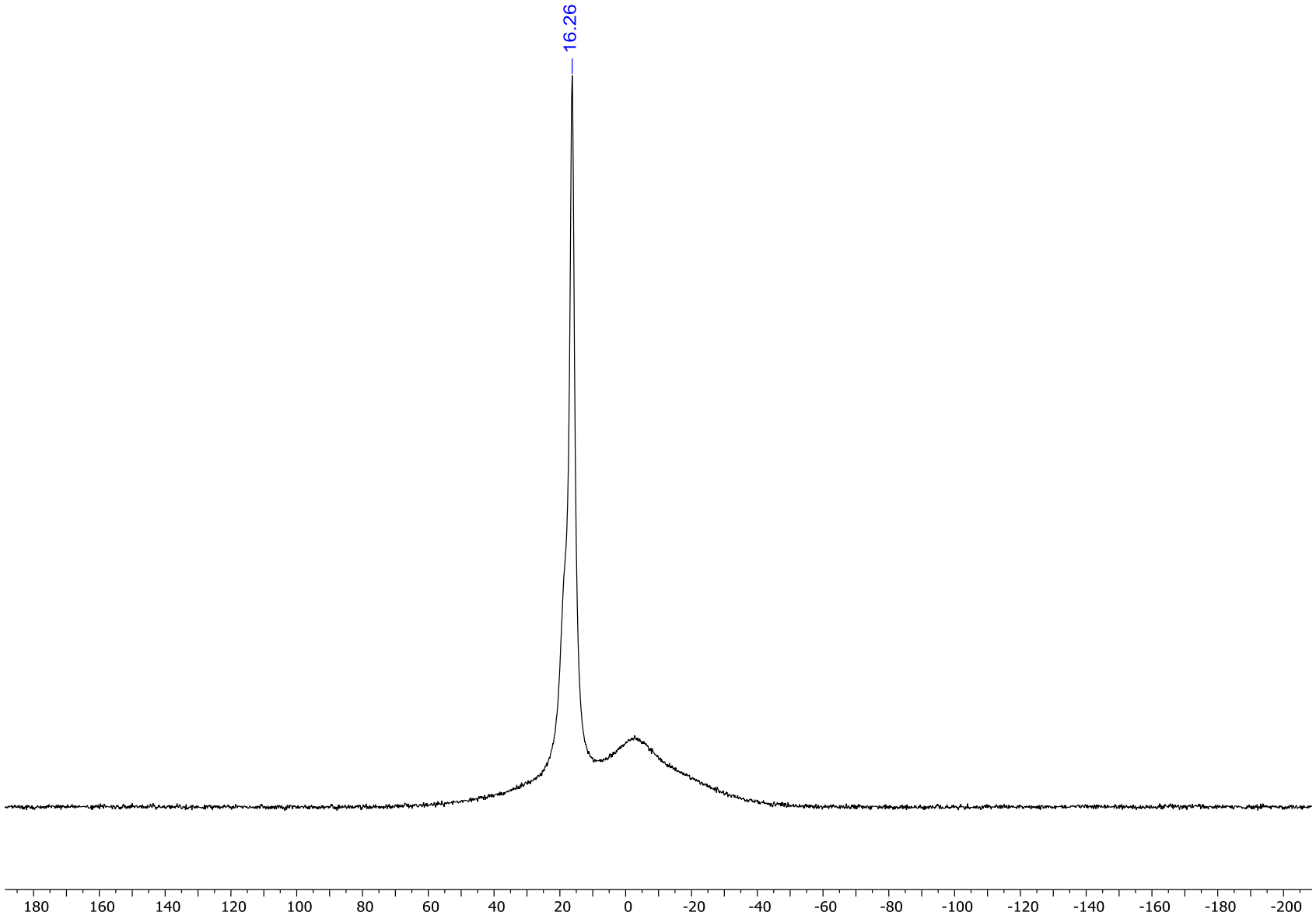


Figure S11: **^{19}F NMR** (376.5 MHz, $CDCl_3$) spectrum of tris(4-fluorophenyl)borate (**3**).

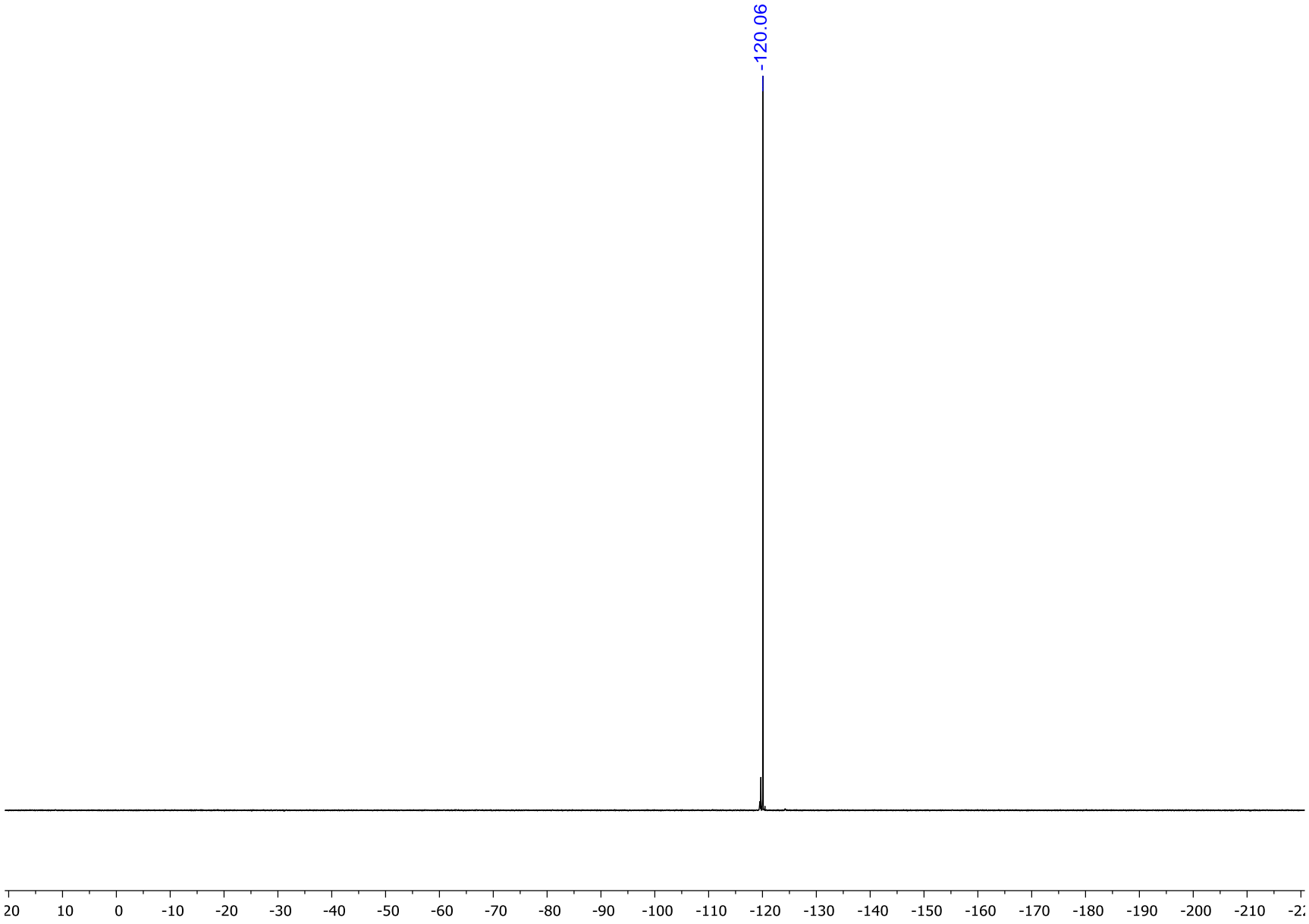


Figure S12: **^{13}C NMR** (100.6 MHz, $CDCl_3$) spectrum of tris(4-fluorophenyl)borate (**3**).

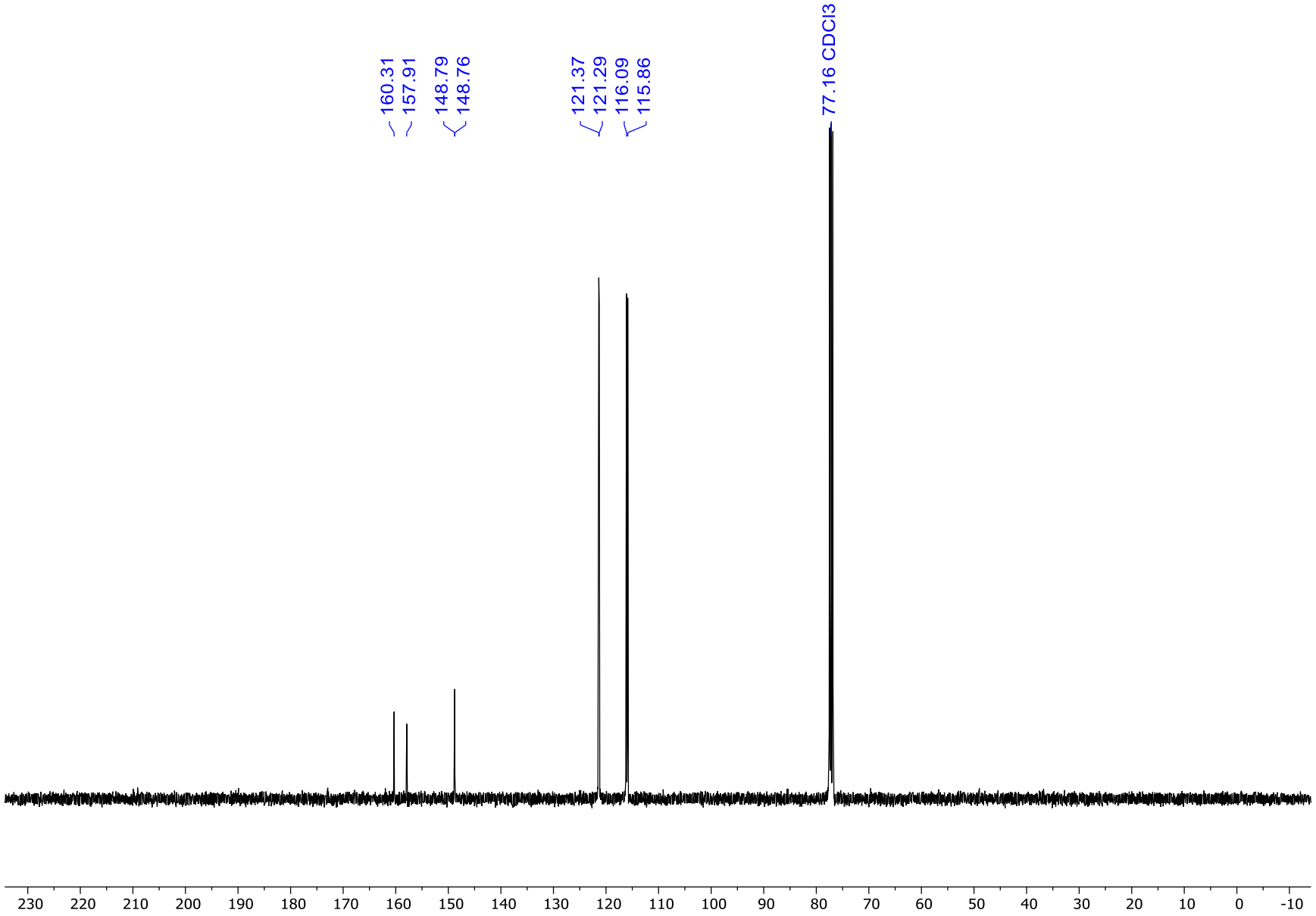


Figure S13: **^{1}H NMR** (400.1 MHz, $CDCl_3$) spectrum of tris(2,4-difluorophenyl)borate (**4**).

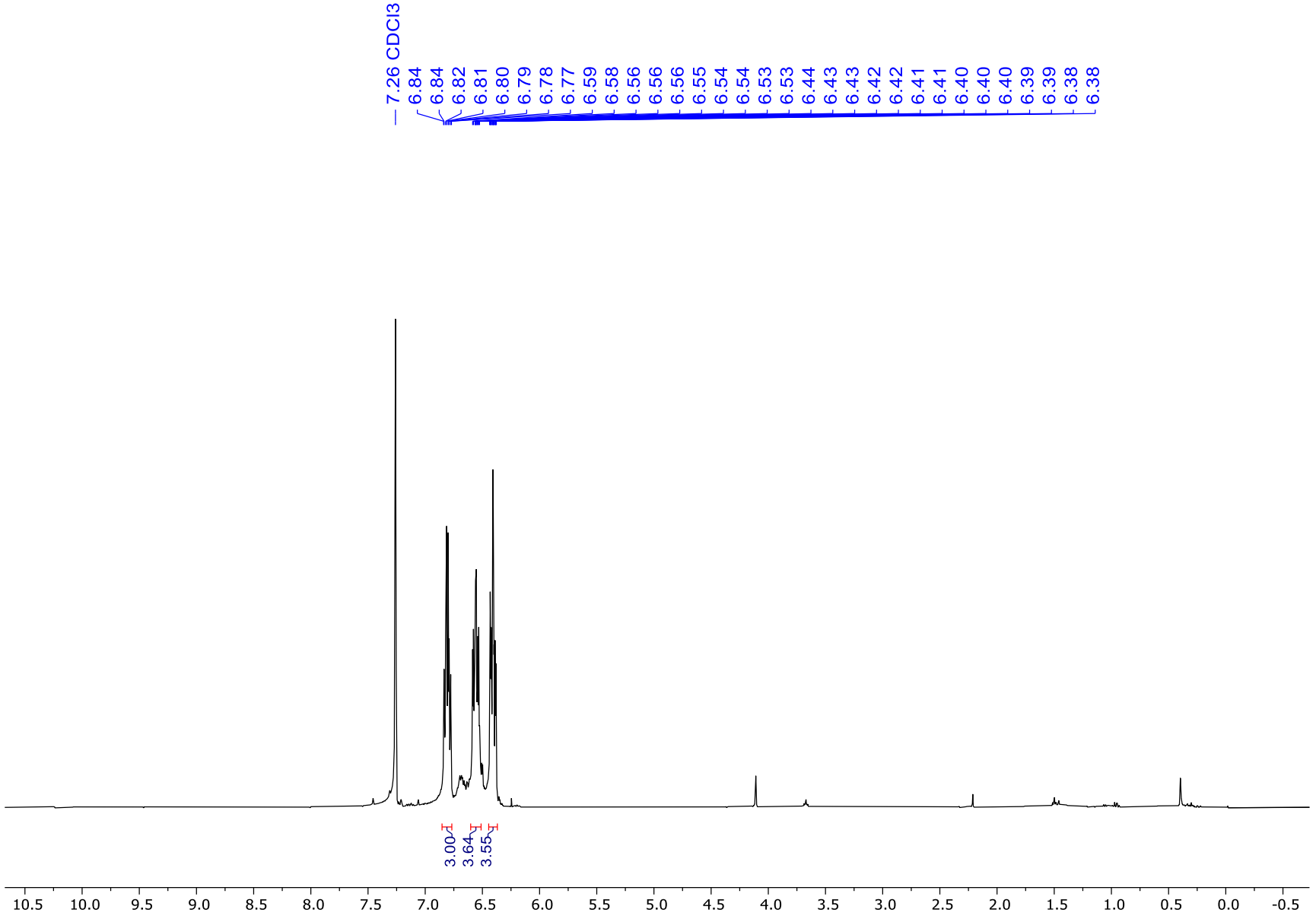


Figure S14: **^{11}B NMR** (128.4 MHz, $CDCl_3$) spectrum of tris(2,4-difluorophenyl)borate (**4**).

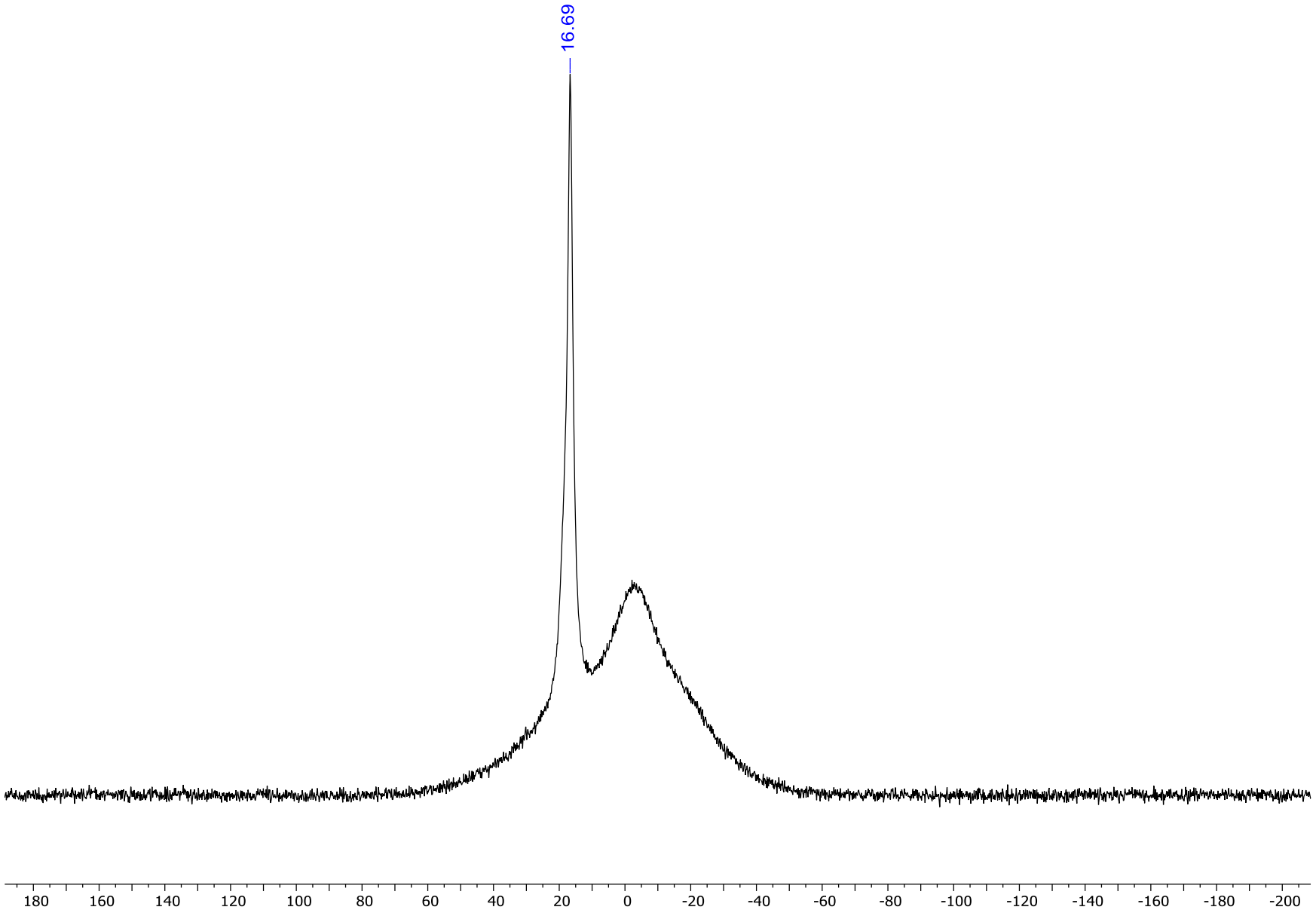


Figure S15: **^{19}F NMR** (376.5 MHz, $CDCl_3$) spectrum of tris(2,4-difluorophenyl)borate (**4**).

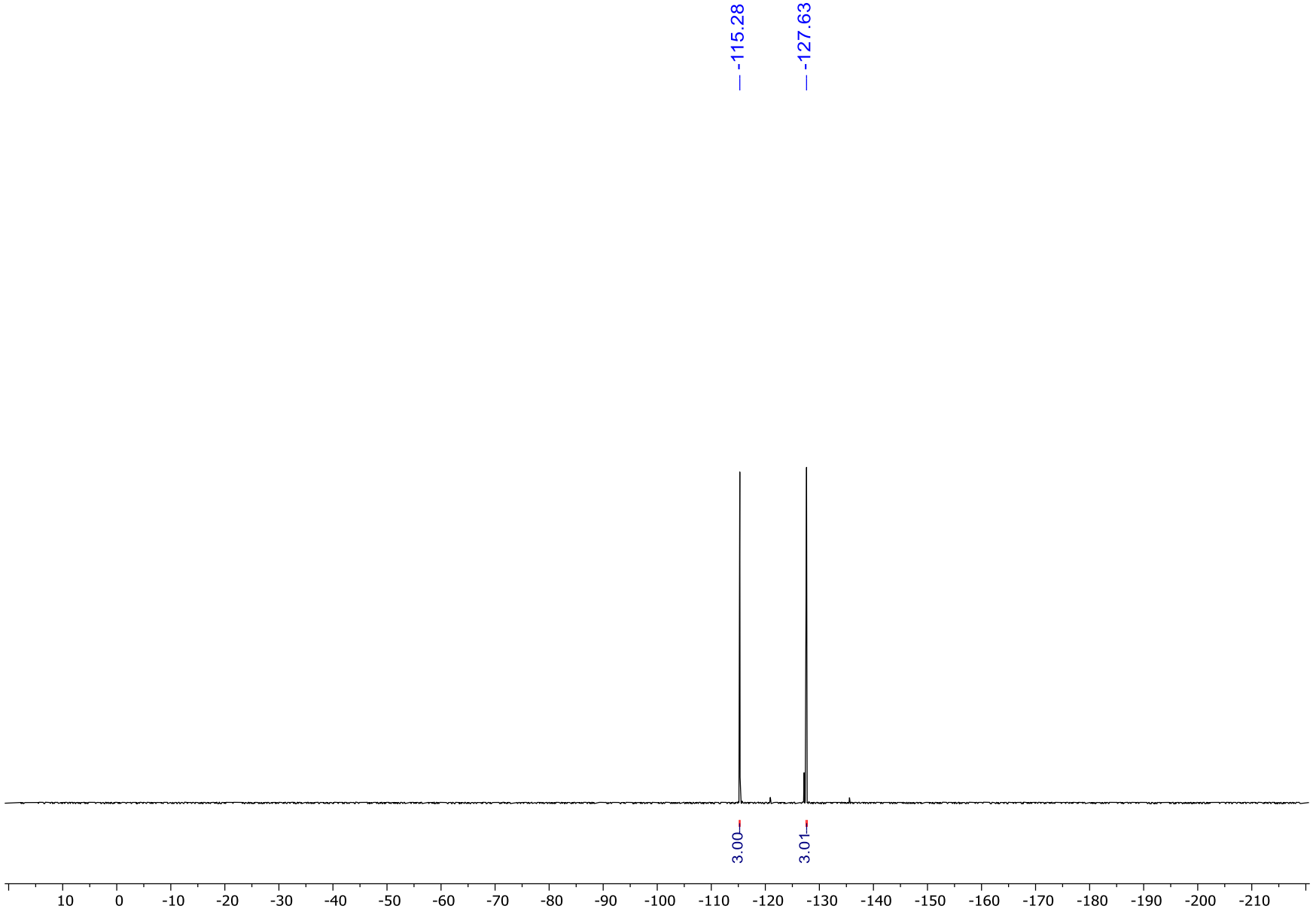


Figure S16: **^{13}C NMR** (100.6 MHz, $CDCl_3$) spectrum of tris(2,4-difluorophenyl)borate (**4**).

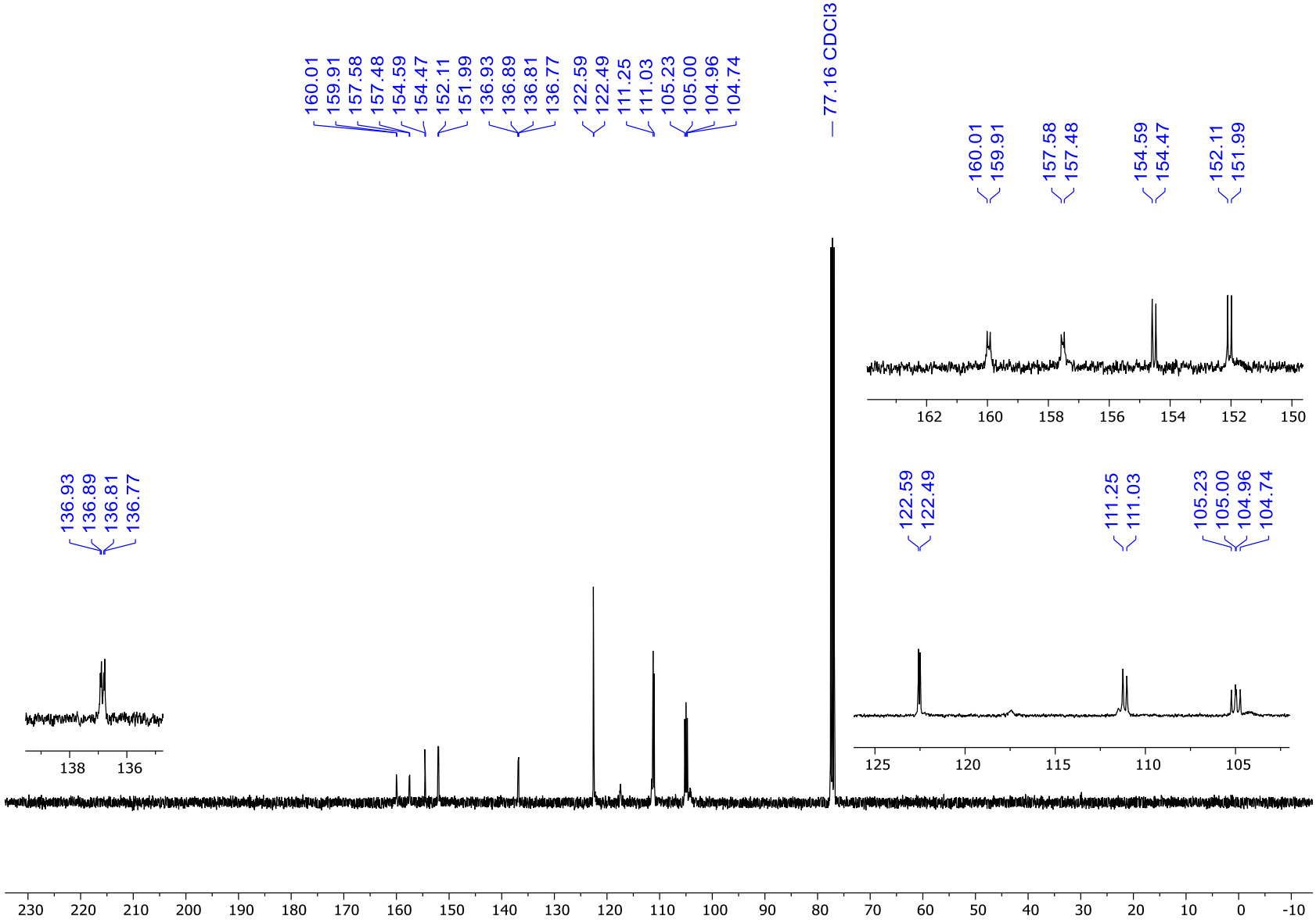


Figure S17: **^{1}H NMR** (400.1 MHz, $CDCl_3$) spectrum of tris(3,5-difluorophenyl)borate (**5**).

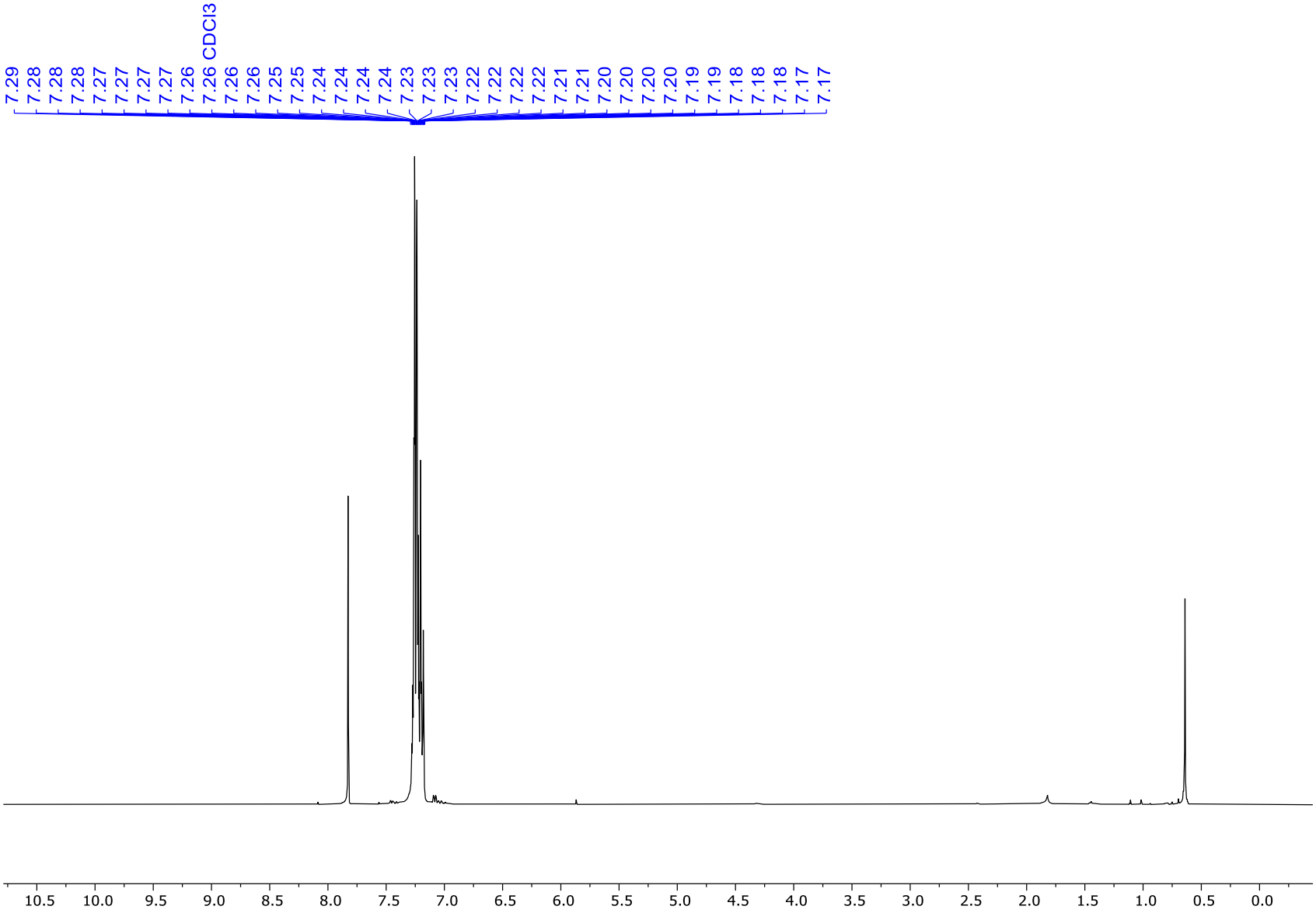


Figure S18: **^{11}B NMR** (128.4 MHz, $CDCl_3$) spectrum of tris(3,5-difluorophenyl)borate (**5**).

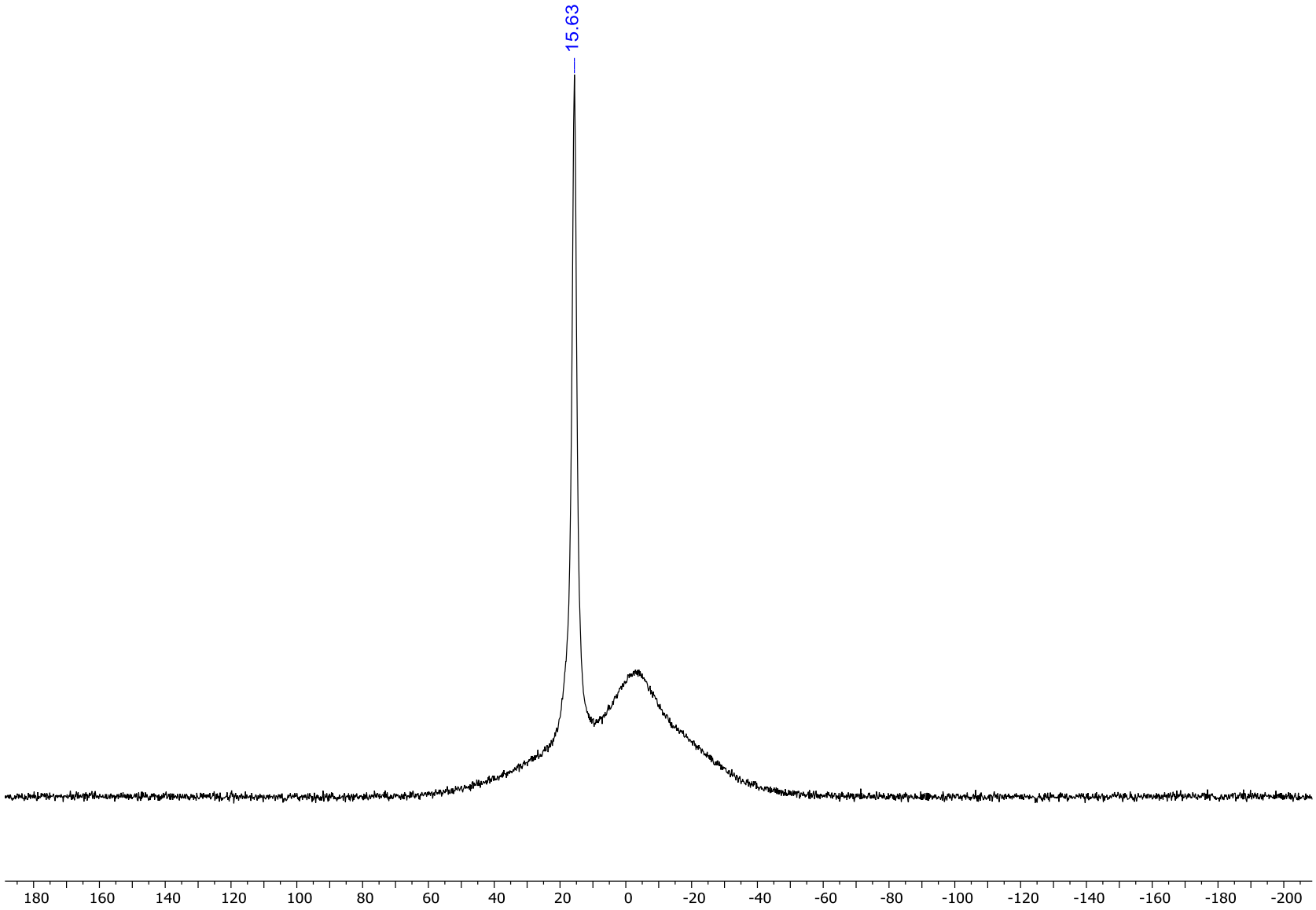


Figure S19: **^{19}F NMR** (376.5 MHz, $CDCl_3$) spectrum of tris(3,5-difluorophenyl)borate (**5**).

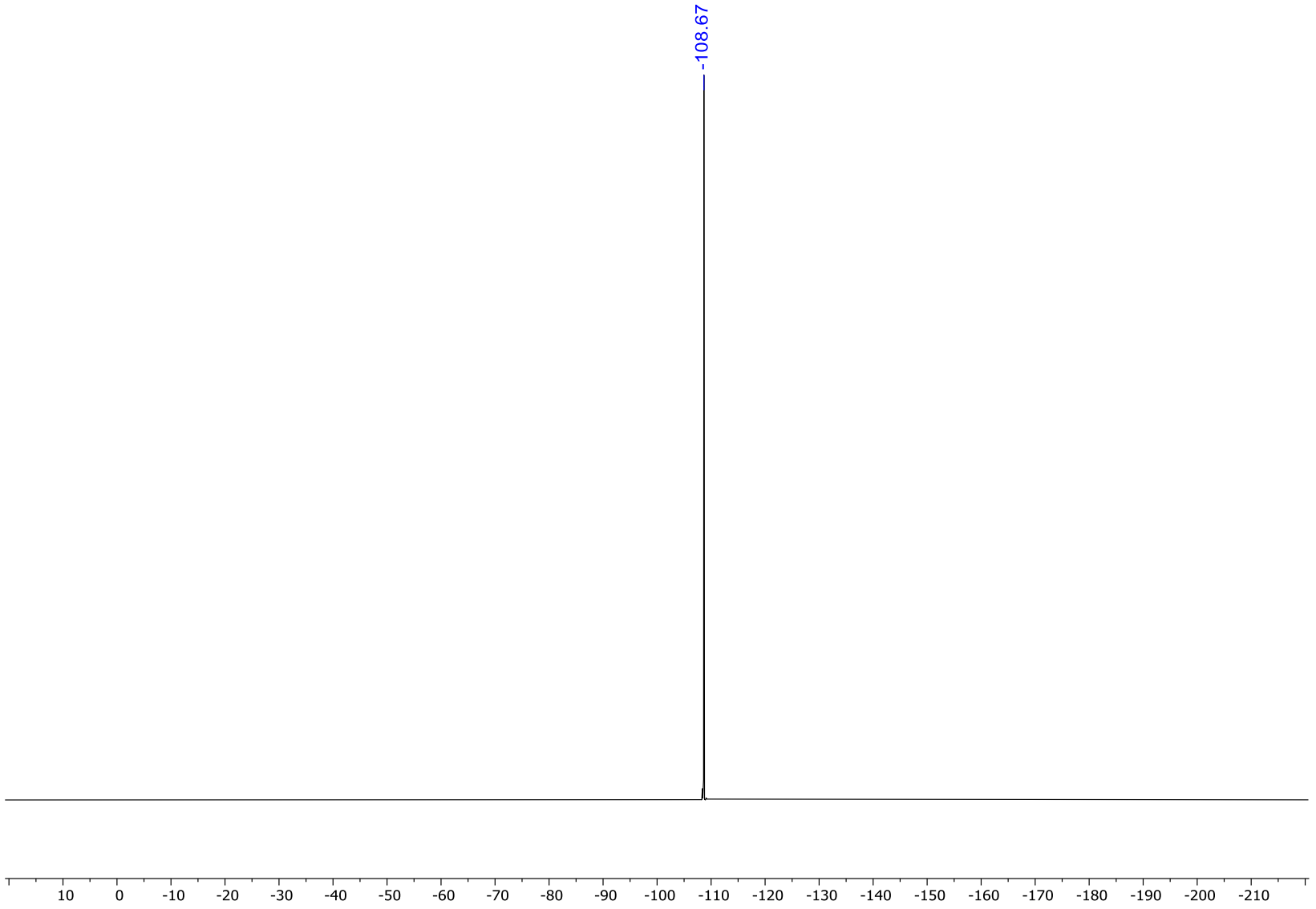


Figure S20: **^{13}C NMR** (100.6 MHz, $CDCl_3$) spectrum of tris(3,5-difluorophenyl)borate (**5**).

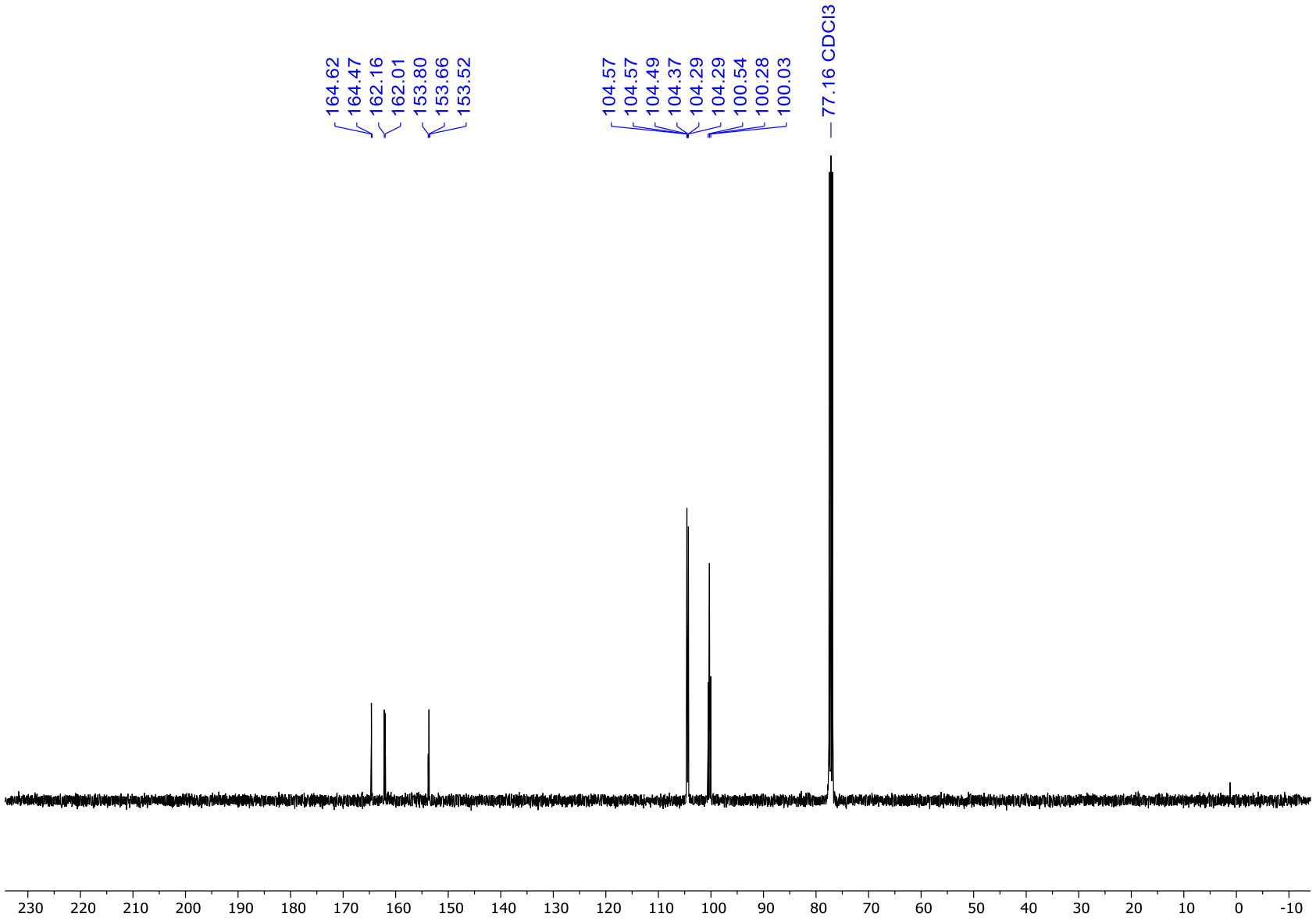


Figure S21: **^{1}H NMR** (400.1 MHz, $CDCl_3$) spectrum of tris(2,3,4-trifluorophenyl)borate (**6**)

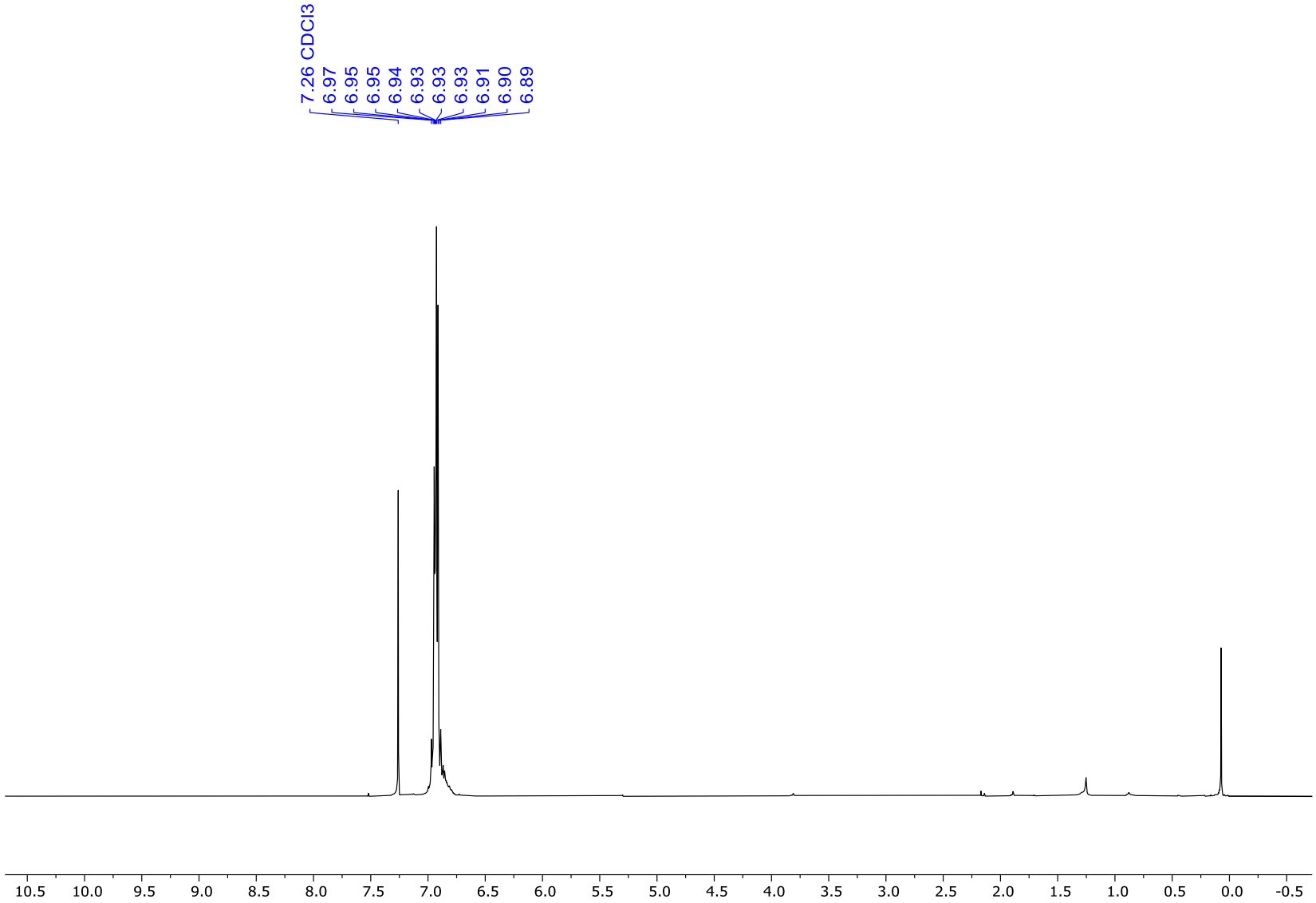


Figure S22: **^{11}B NMR** (128.4 MHz, $CDCl_3$) spectrum of tris(2,3,4-trifluorophenyl)borate (**6**).

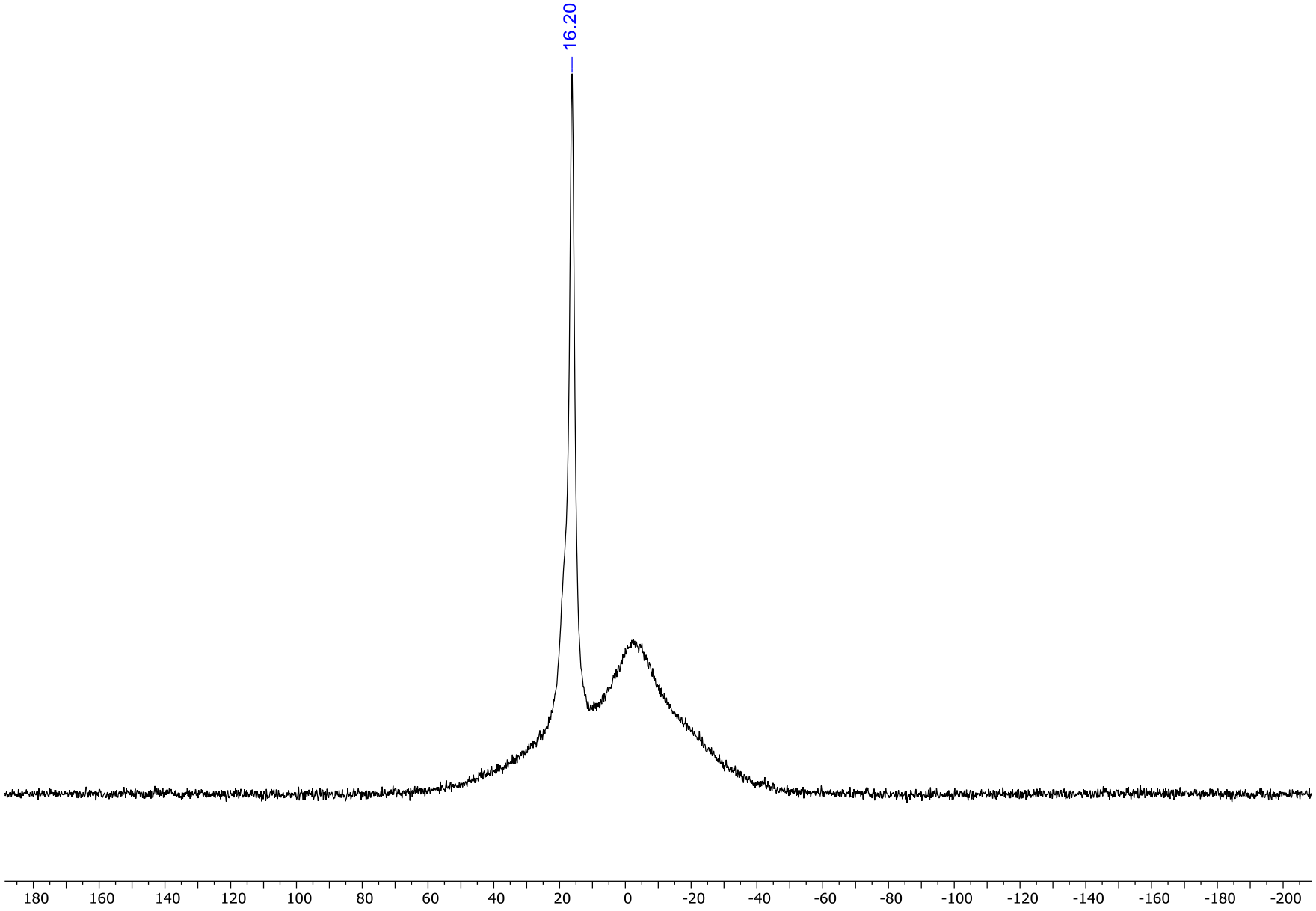


Figure S23: **^{19}F NMR** (376.5 MHz, $CDCl_3$) spectrum of tris(2,3,4-trifluorophenyl)borate (**6**).

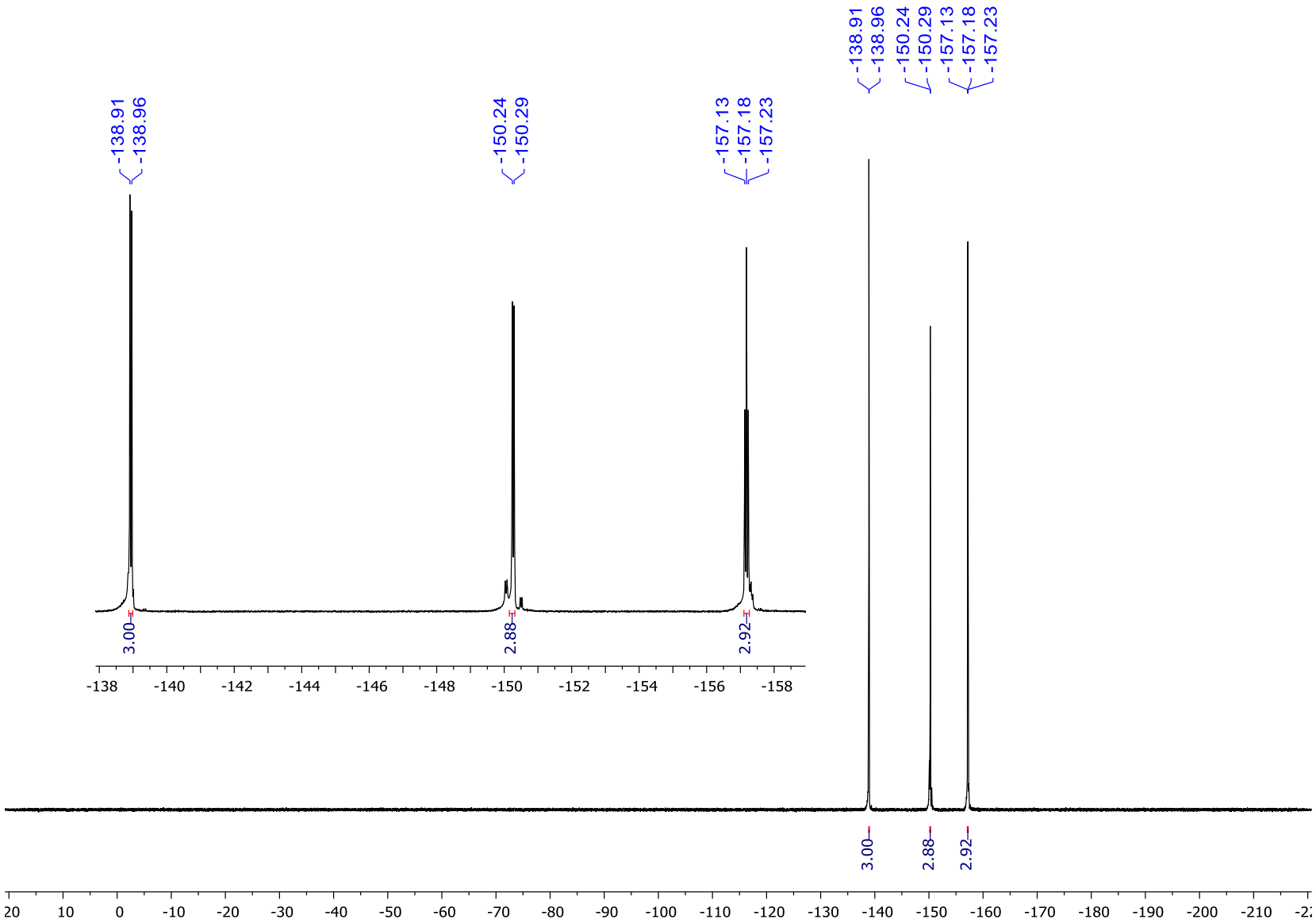


Figure S24: **^{13}C NMR** (100.1 MHz, $CDCl_3$) spectrum of tris(2,3,4-trifluorophenyl)borate (**6**).

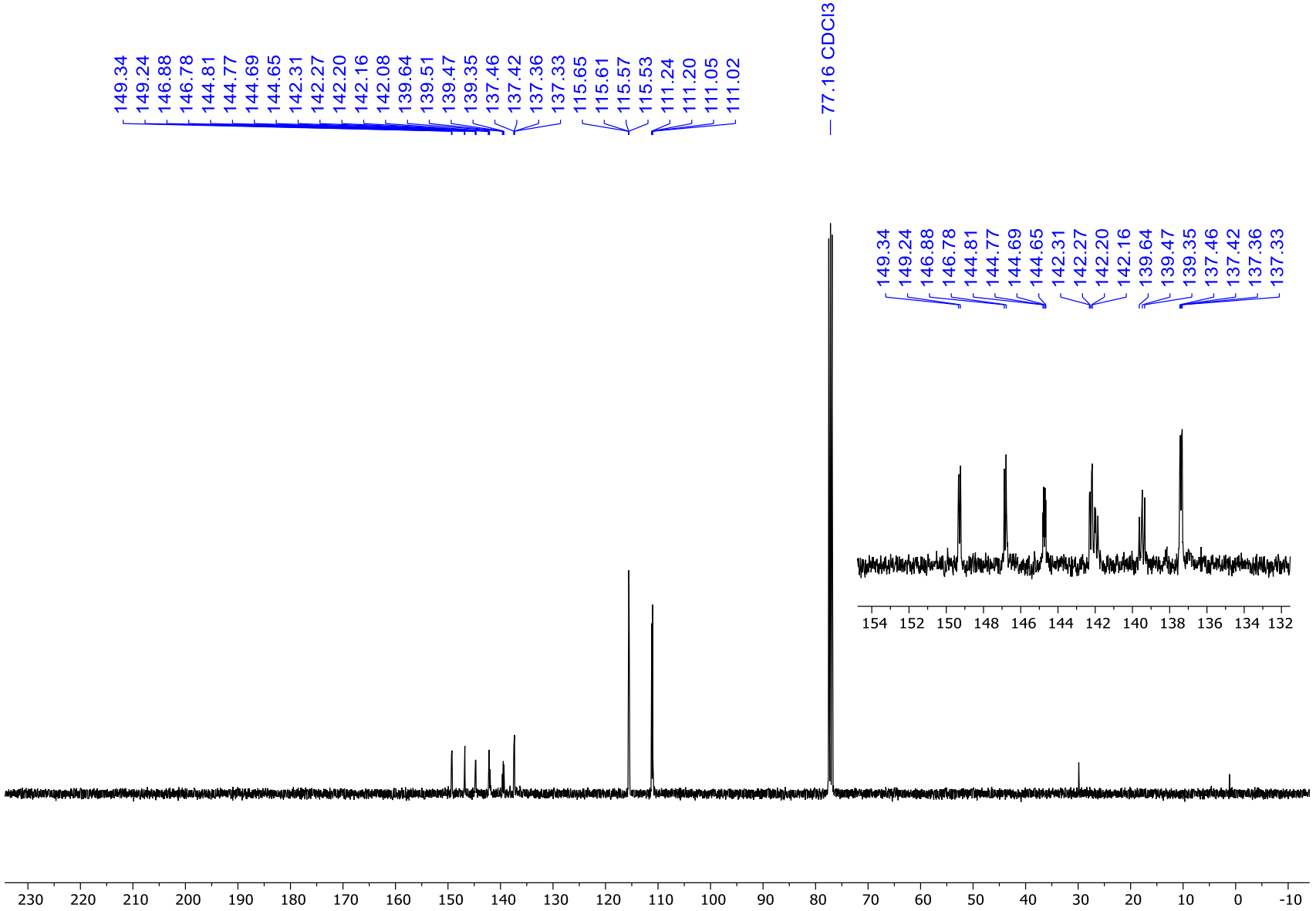


Figure S25: **^{1}H NMR** (400.1 MHz, $CDCl_3$) spectrum of tris(2,4,6-trifluorophenyl)borate (**7**).

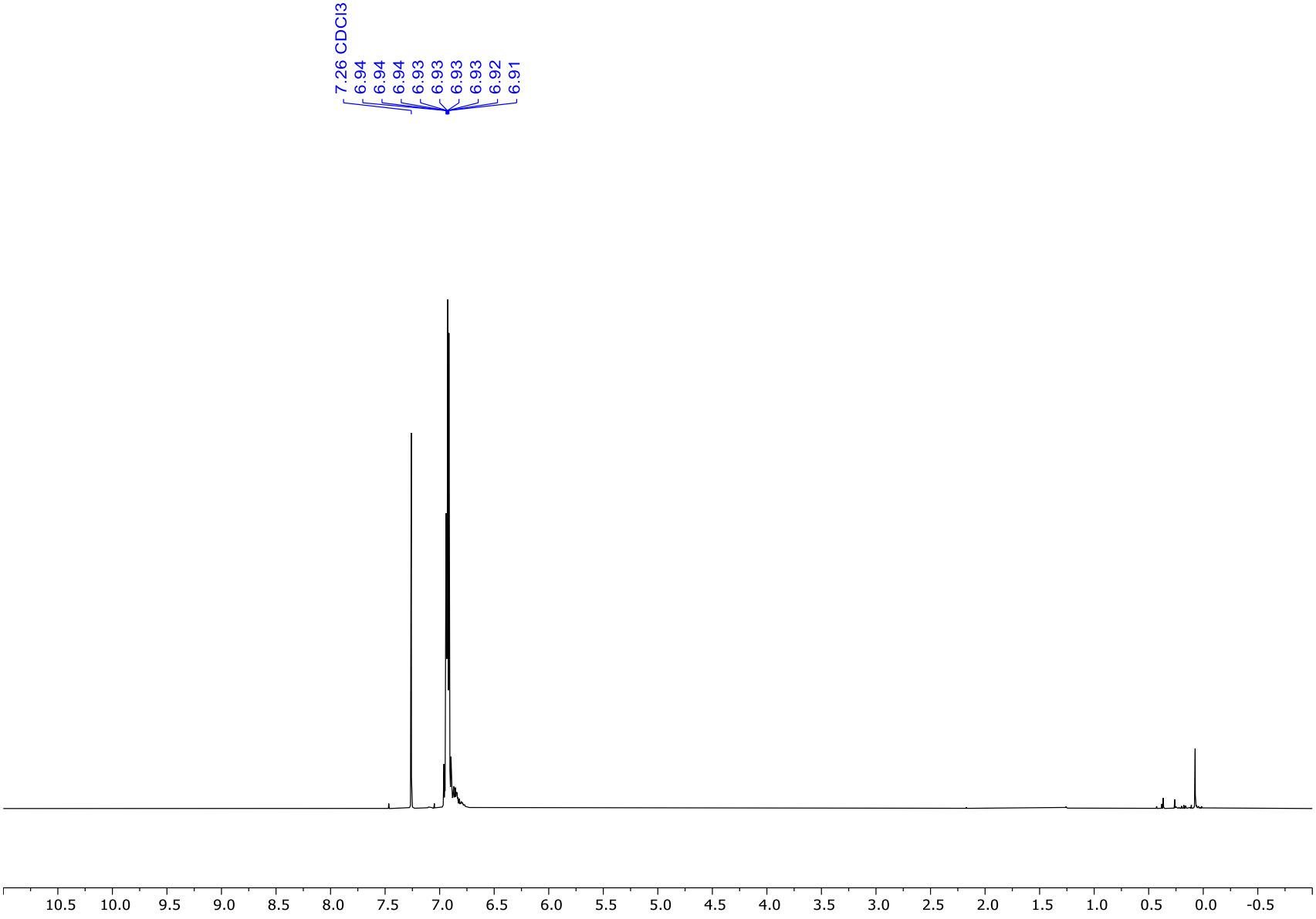


Figure S26: **^{11}B NMR** (125.8 MHz, $CDCl_3$) spectrum of tris(2,4,6-trifluorophenyl)borate (**7**).

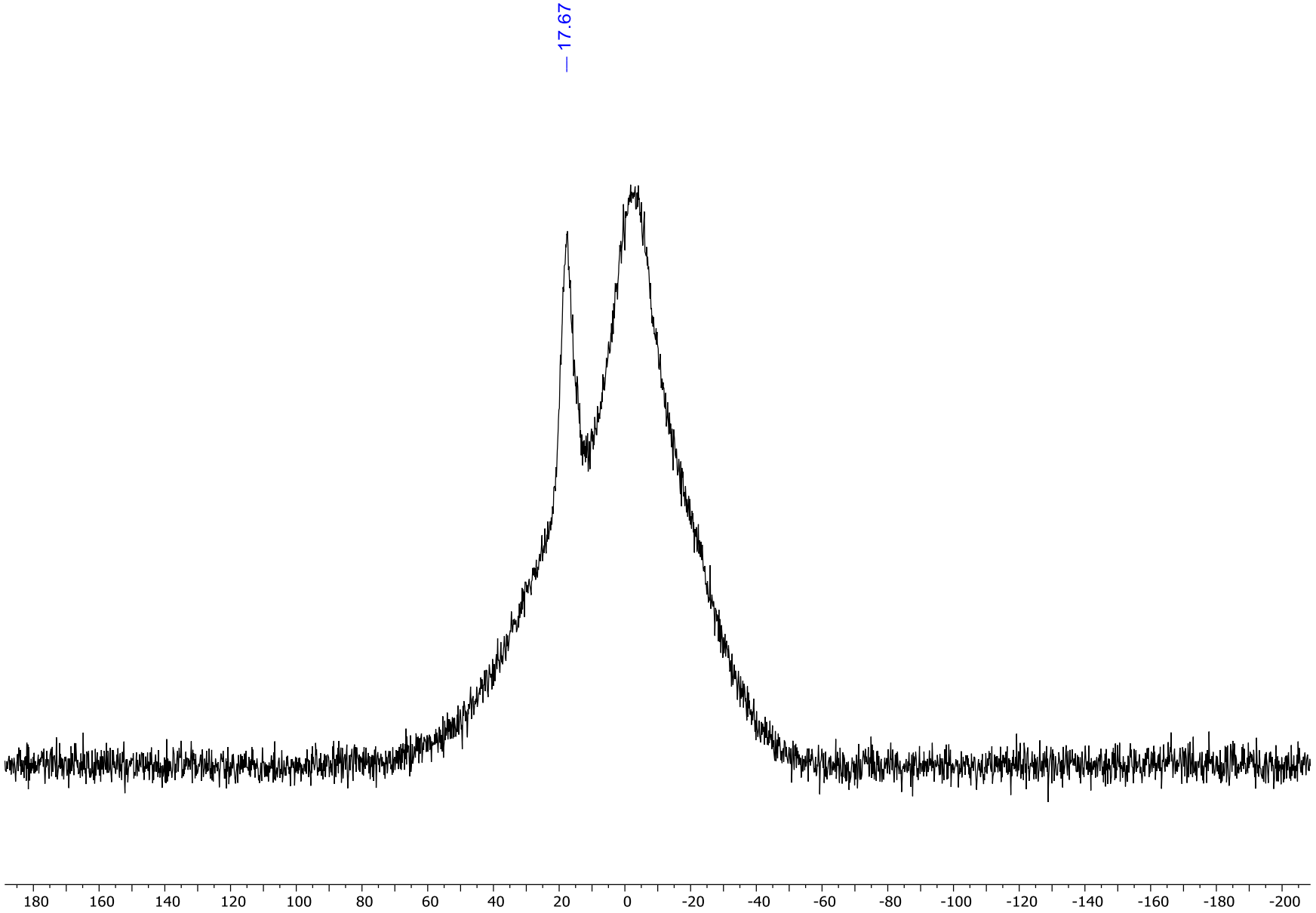


Figure S27: **^{19}F NMR** (470.2 MHz, $CDCl_3$) spectrum of tris(2,4,6-trifluorophenyl)borate (**7**).

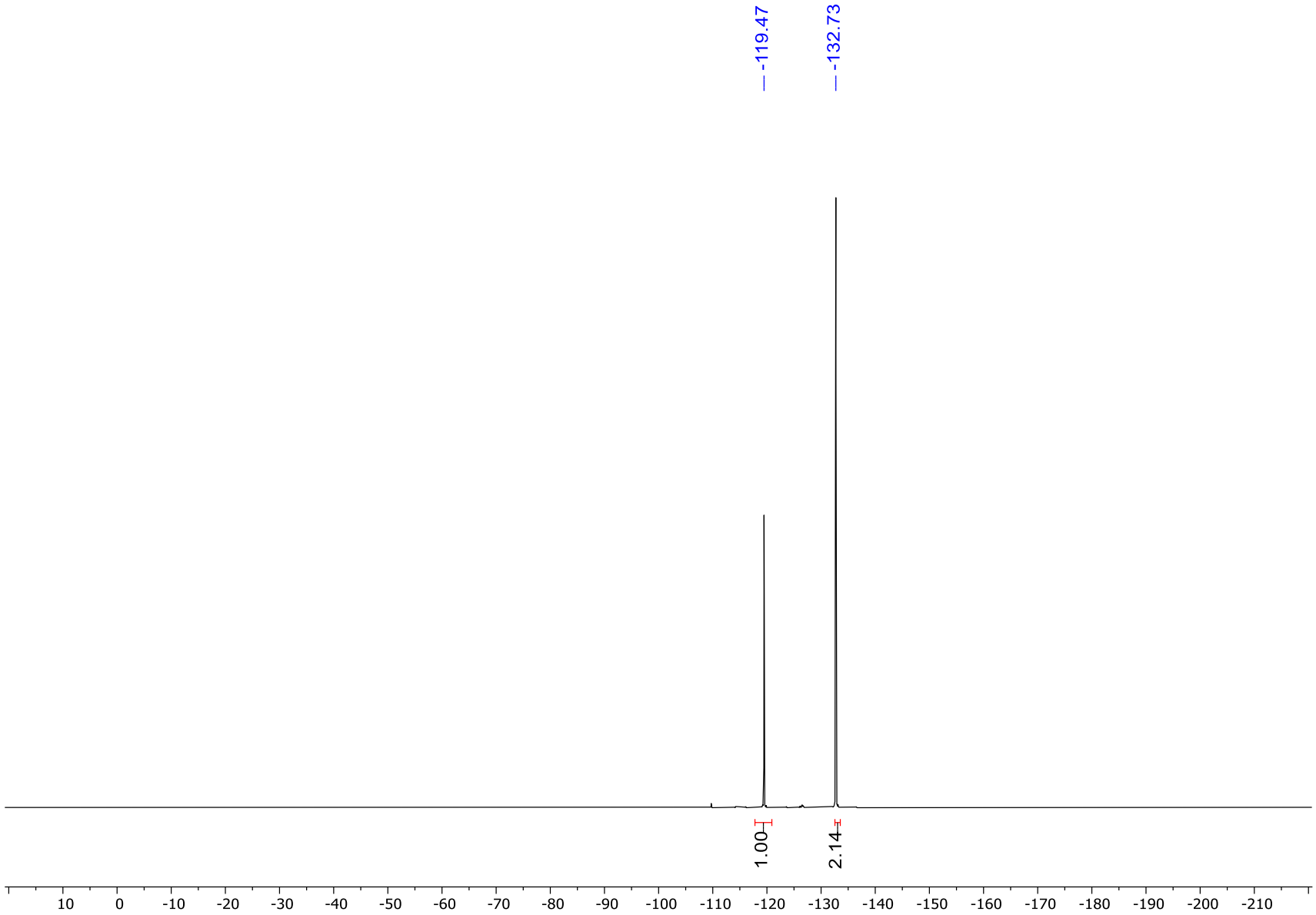


Figure S28: **^{13}C NMR** (125.8 MHz, $CDCl_3$) spectrum of tris(2,4,6-trifluorophenyl)borate (**7**).

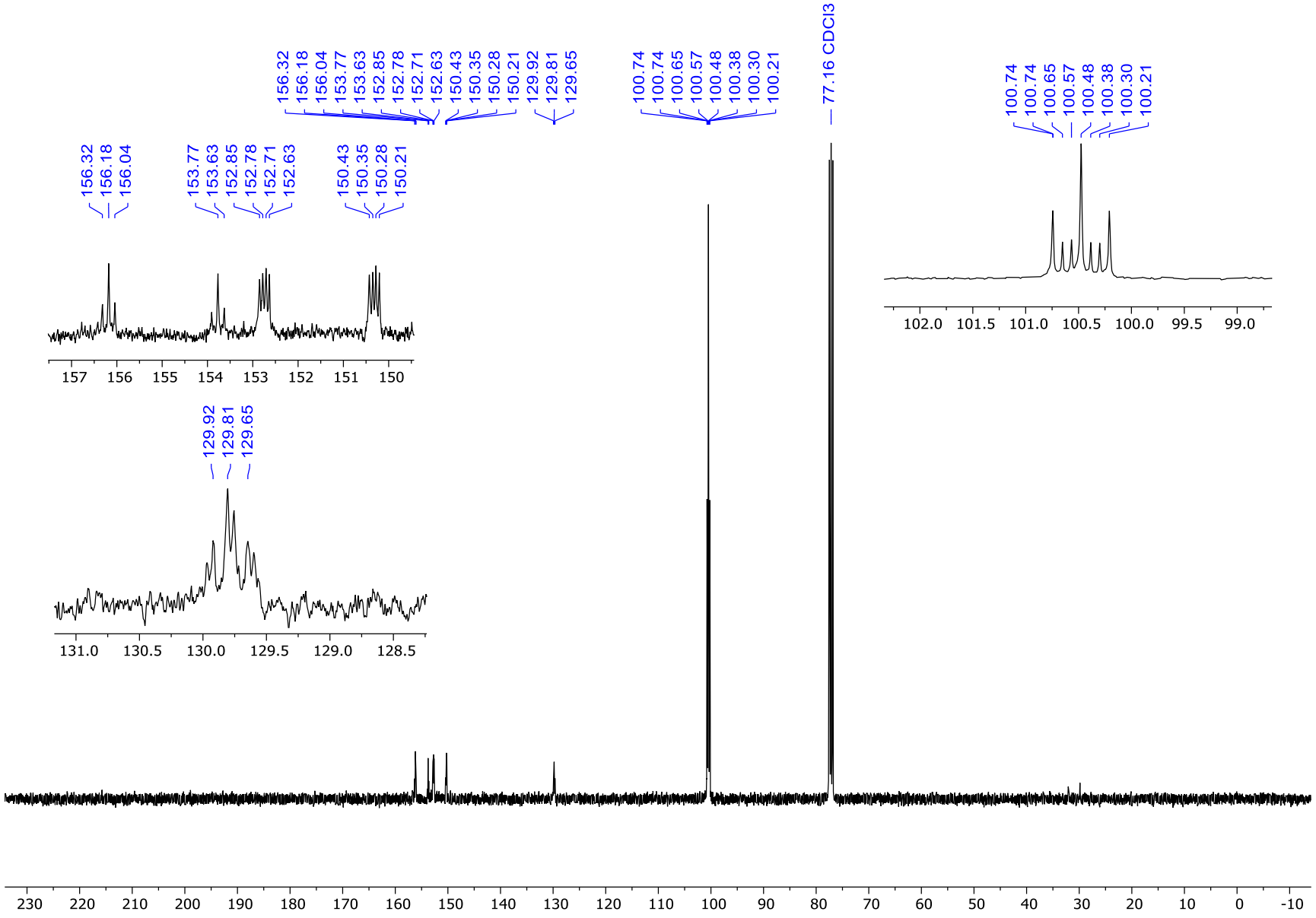


Figure S29: **^{1}H NMR** (400.1 MHz, $CDCl_3$) spectrum of tris(3,4,5-trifluorophenyl)borate (**8**).

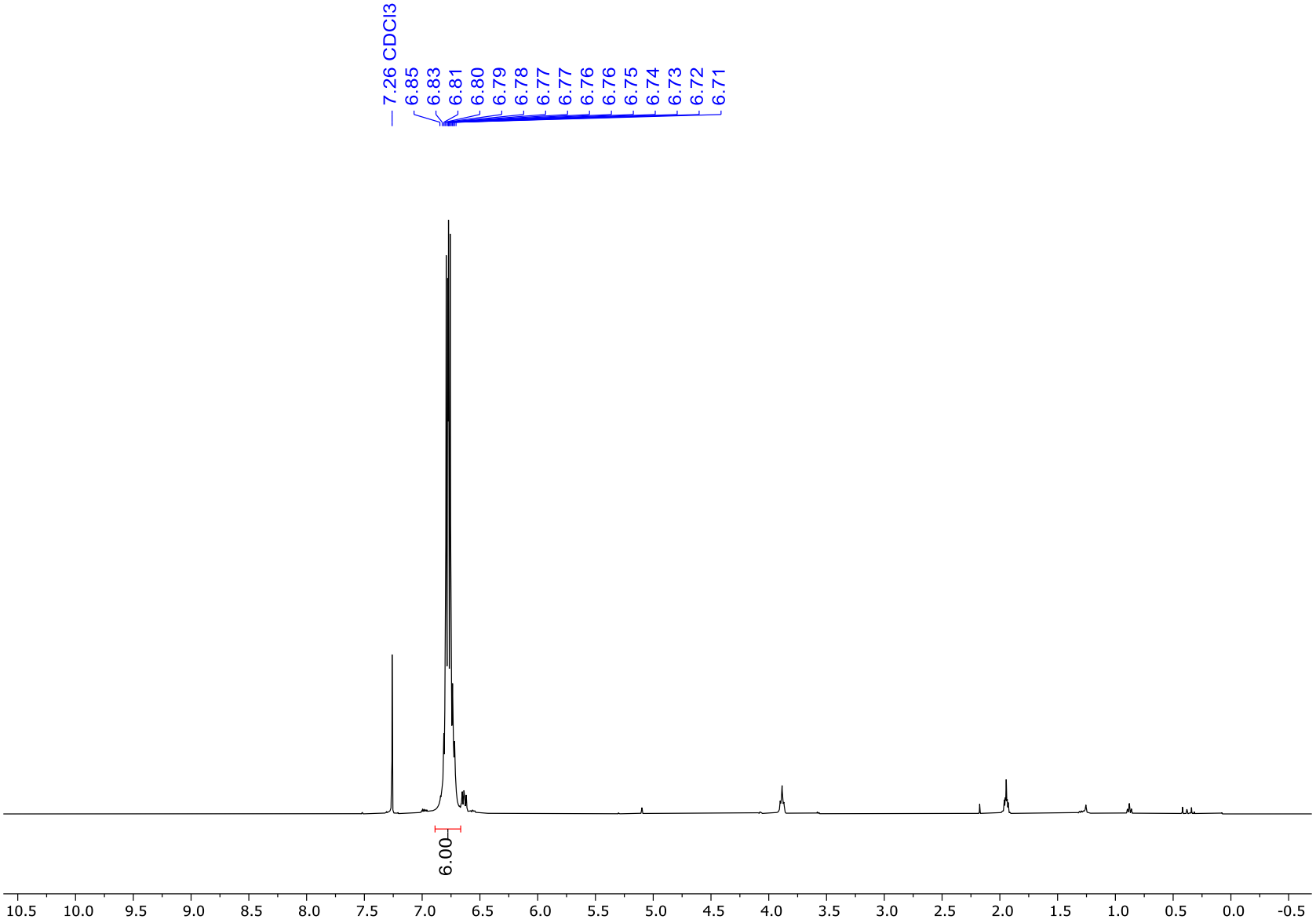


Figure S30: **^{11}B NMR** (128.4 MHz, $CDCl_3$) spectrum of tris(3,4,5-trifluorophenyl)borate (**8**).

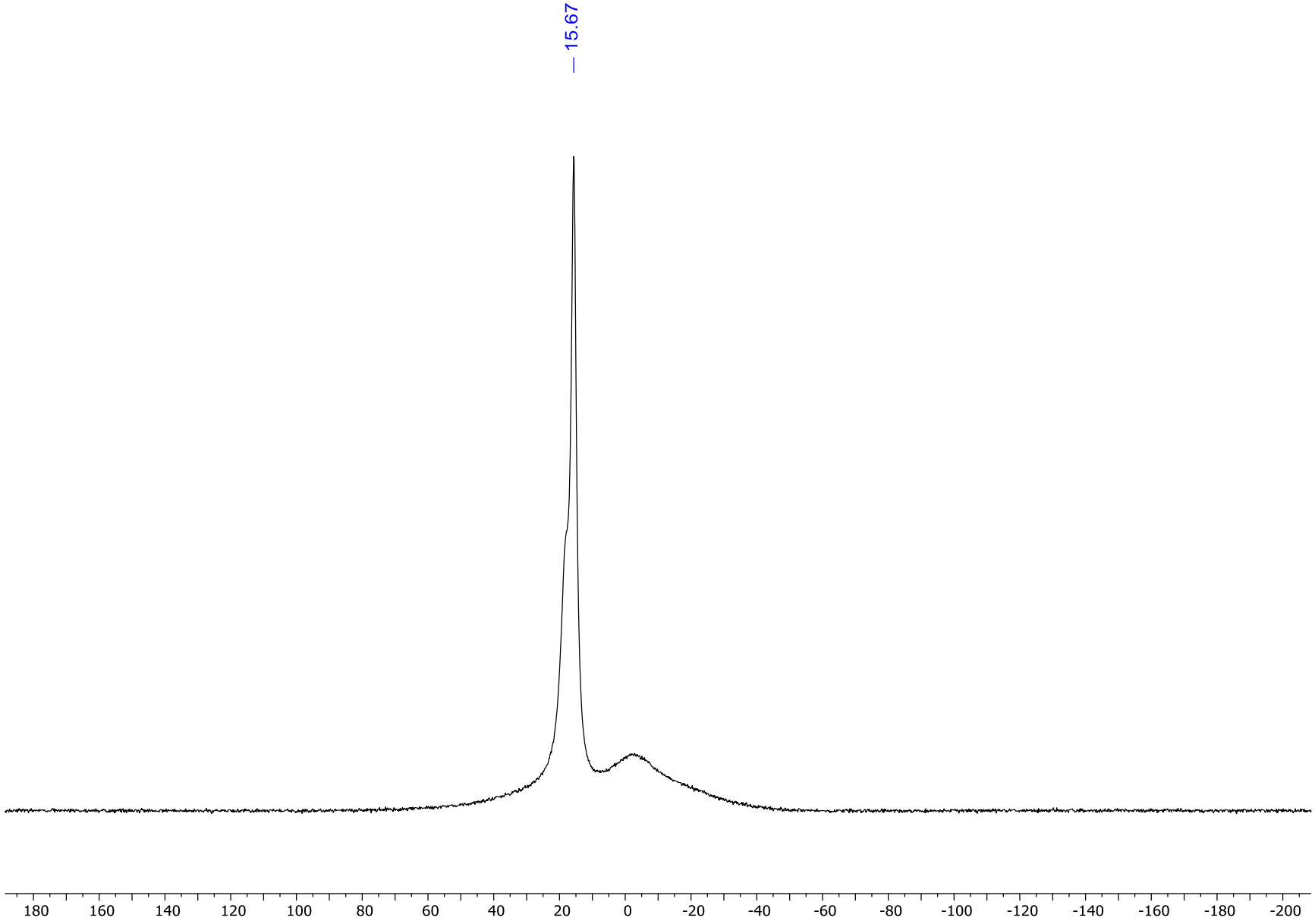


Figure S31: **^{19}F NMR** (376.5 MHz, $CDCl_3$) spectrum of tris(3,4,5-trifluorophenyl)borate (**8**).

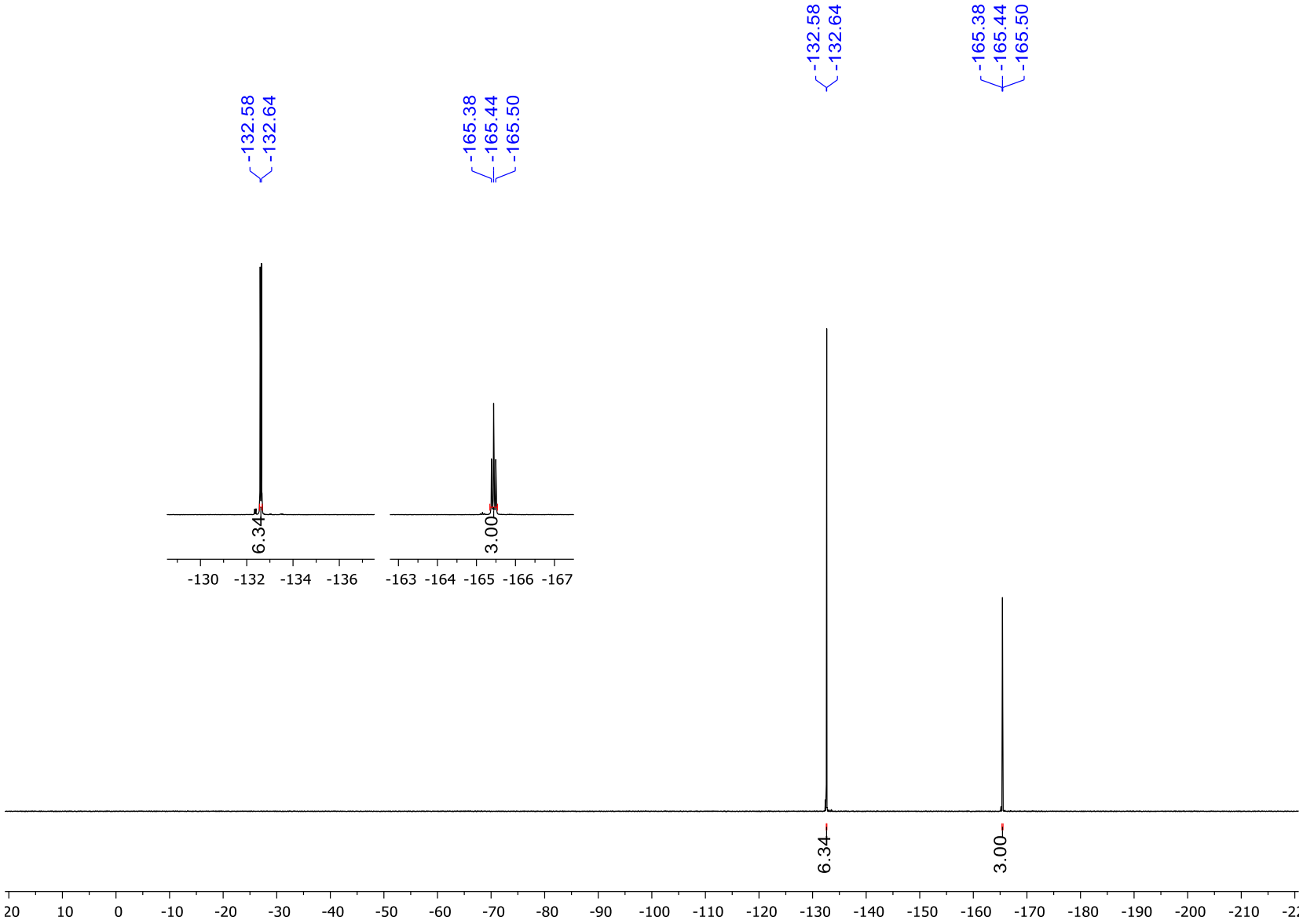
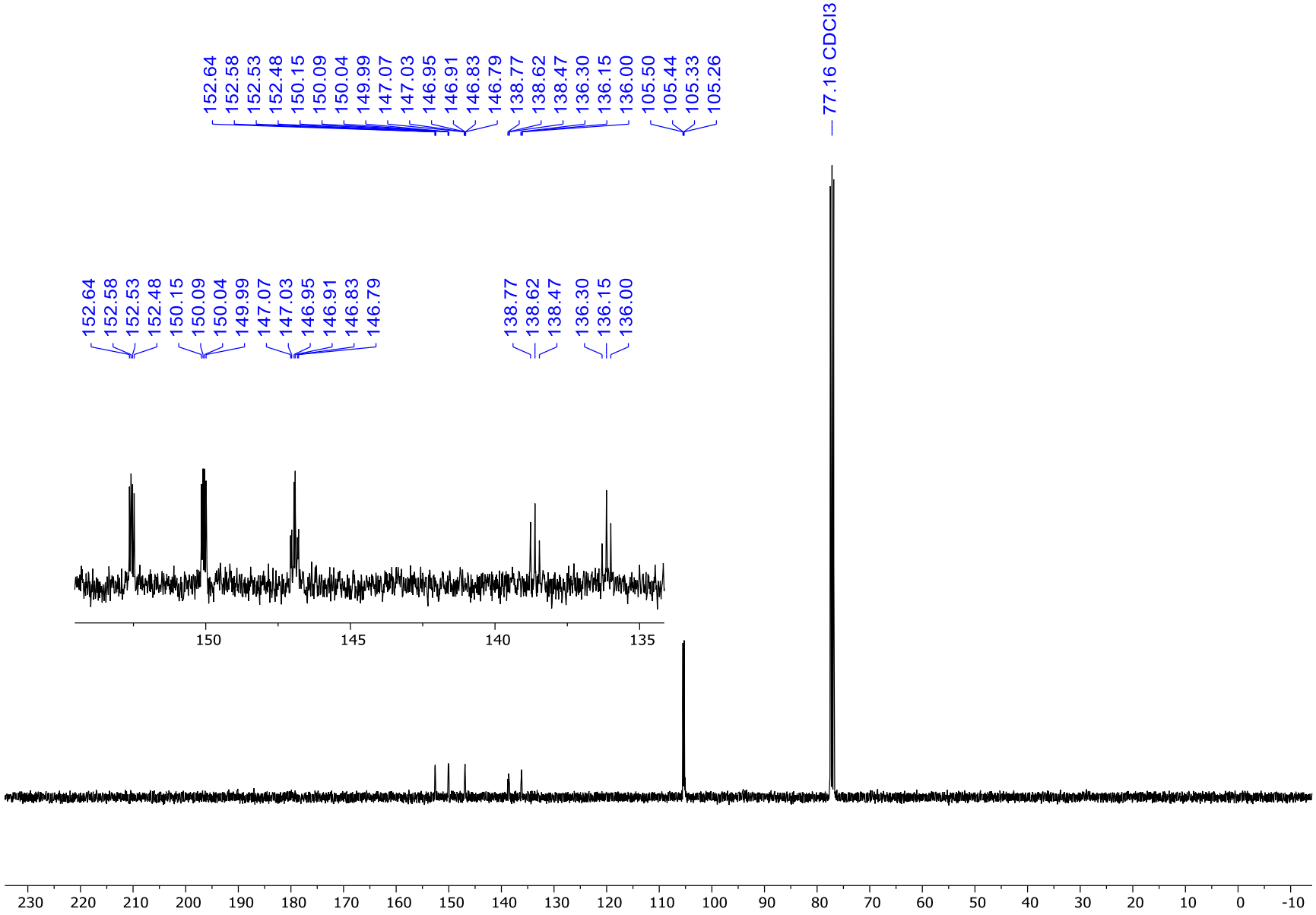


Figure S32: **^{13}C NMR** (100.6 MHz, $CDCl_3$) spectrum of tris(3,4,5-trifluorophenyl)borate (**8**).



4. Determination of the Lewis acidity of fluorinated triaryl borates

4.1 Gutmann-Beckett method[45]

General procedure B: The borate (1.0 equiv.) was dissolved in $CDCl_3$ (0.5 mL) and Et_3PO (0.6 equiv.) was added. A capillary containing PPh_3 in $CDCl_3$ was added to the solution as internal standard. The ^{31}P NMR chemical shift of the PPh_3 in $CDCl_3$ was calibrated to δ = -5.21 ppm according to O. M. Demchuk *et al*.[6] The ^{31}P chemical shift of the unsolvated Et_3PO referenced to PPh_3 is 52.5 ppm. Δδ ^{31}P describes the induced shift of the ^{31}P NMR signal of Et_3PO upon coordination to a Lewis acid.

Table S1. Gutmann-Beckett ^{31}P NMR signals of compounds **1** – **8.**

Compound	^{31}P Et_3PO [ppm]	Δδ ^{31}P Et_3PO [ppm]
$B(2\text{-}F_1H_4C_6O)_3$ (**1**)	76.3	23.8
$B(3\text{-}F_1H_4C_6O)_3$ (**2**)	74.5	22.0
$B(4\text{-}F_1H_4C_6O)_3$ (**3**)	66.6	14.1
$B(2,4\text{-}F_2H_3C_6O)_3$ (**4**)	76.2	23.7
$B(3,5\text{-}F_2H_3C_6O)_3$ (**5**)	78.9	26.4
$B(2,3,4\text{-}F_3H_2C_6O)_3$ (**6**)	79.6	27.1
$B(2,4,6\text{-}F_3H_2C_6O)_3$ (**7**)	79.6	27.1
$B(3,4,5\text{-}F_3H_2C_6O)_3$ (**8**)	79.1	26.6

*$B(2\text{-}F_1H_4C_6O)_3$ (**1**):*

According to *General Procedure B*, using **1** (20.0 mg, 0.058 mmol, 1.0 equiv.) and Et_3PO (4.68 mg, 0.034 mmol, 0.6 equiv.). **^{31}P NMR** (202.5 MHz, $CDCl_3$) δ: 76.3 ppm (s).

*$B(3\text{-}F_1H_4C_6O)_3$ (**2**):*

According to *General Procedure B*, using **2** (20.0 mg, 0.058 mmol, 1.0 equiv.) and Et_3PO (4.68 mg, 0.034 mmol, 0.6 equiv.). **^{31}P NMR** (202.5 MHz, $CDCl_3$) δ: 74.5 ppm (s).

*$B(4\text{-}F_1H_4C_6O)_3$ (**3**):*

According to *General Procedure B*, using **3** (20.0 mg, 0.058 mmol, 1.0 equiv.) and Et_3PO (4.68 mg, 0.034 mmol, 0.6 equiv.). **^{31}P NMR** (202.5 MHz, $CDCl_3$) δ: 66.6 ppm (s).

*B(2,4-$F_2H_3C_6O)_3$ (**4**):*

According to *General Procedure B*, using **4** (20.0 mg, 0.05 mmol, 1.0 equiv.) and Et_3PO (4.04 mg, 0.026 mmol, 0.6 equiv.). **^{31}P NMR** (202.5 MHz, $CDCl_3$) δ: 76.2 ppm (s).

*B(3,5-$F_2H_3C_6O)_3$ (**5**):*

According to *General Procedure B*, using **5** (20.0 mg, 0.05 mmol, 1.0 equiv.) and Et_3PO (4.04 mg, 0.03 mmol, 0.6 equiv.). **^{31}P NMR** (202.5 MHz, $CDCl_3$) δ: 78.9 ppm (s).

*B(2,3,4-$F_3H_2C_6O)_3$ (**6**):*

According to *General Procedure B*, using **6** (20.0 mg, 0.04 mmol, 1.0 equiv.) and Et_3PO (3.56 mg, 0.026 mmol, 0.6 equiv.). **^{31}P NMR** (202.5 MHz, $CDCl_3$) δ: 79.6 ppm (s).

*B(2,4,6-$F_3H_2C_6O)_3$ (**7**):*

According to *General Procedure B*, using **7** (20.0 mg, 0.04 mmol, 1.0 equiv.) and Et_3PO (3.56 mg, 0.026 mmol, 0.6 equiv.). **^{31}P NMR** (202.5 MHz, $CDCl_3$) δ: 79.6 ppm (s).

*B(3,4,5-$F_3H_2C_6O)_3$ (**8**):*

According to *General Procedure B*, using **8** (20.0 mg, 0.04 mmol, 1.0 equiv.) and Et_3PO (3.56 mg, 0.026 mmol, 0.6 equiv.). **^{31}P NMR** (202.5 MHz, $CDCl_3$) δ: 79.1 ppm (s).

4.2 Childs Method[7]

General procedure C: The borate (1.0 equiv.) was dissolved in $CDCl_3$ (0.5 mL) and *trans*-crotonaldehyde (0.6 equiv.) was added. The spectrum was referenced to $CDCl_3$. The ^1H chemical shift of H3 of the unsolvated crotonaldehyde referenced to $CDCl_3$ is 6.85 ppm. $\Delta\delta\ ^1H$ describes the induced shift of the ^1H NMR signal of H3 of *trans*-crotonaldehyde upon coordination to a Lewis acid.

Table S2. Childs ^1H NMR signals of compounds **1** – **8.**

Compound	^1H H3 crotonaldehyde [ppm]	$\Delta\delta\ ^1H$ H3 crotonaldehyde [ppm]
$B(2\text{-}FH_4C_6O)_3$ (**1**)	6.87	0.02
$B(3\text{-}FH_4C_6O)_3$ (**2**)	Signals of **2** and the H3 proton of crotonaldehyde are overlapping. Therefore, Δδ could not be determined.	
$B(4\text{-}FH_4C_6O)_3$ (**3**)	6.87	0.02
$B(2,4\text{-}F_2H_3C_6O)_3$ (**4**)	Signals of **4** and the H3 proton of crotonaldehyde are overlapping. Therefore, Δδ could not be determined.	
$B(3,5\text{-}F_2H_3C_6O)_3$ (**5**)	6.87	0.02
$B(2,3,4\text{-}F_3H_2C_6O)_3$ (**6**)	6.88	0.03
$B(2,4,6\text{-}F_3H_2C_6O)_3$ (**7**)	6.88	0.03
$B(3,4,5\text{-}F_3H_2C_6O)_3$ (**8**)	6.88	0.03

*$B(2\text{-}F_1H_4C_6O)_3$ (**1**):*

According to *General Procedure C*, using **1** (20.0z mg, 0.058 mmol, 1.0 equiv.) and *trans*-crotonaldehyde (2.44 mg, 0.034 mmol, 0.6 equiv.). **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ: 6.87 ppm (m).

*$B(3\text{-}F_1H_4C_6O)_3$ (**2**):*

According to *General Procedure C*, using **2** (20.0 mg, 0.05 mmol, 1.0 equiv.) and *trans*-crotonaldehyde (2.4 mg, 0.03 mmol, 0.6 equiv.). **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ: Not determined.

*$B(4\text{-}F_1H_4C_6O)_3$ (**3**):*

According to *General Procedure C*, using **3** (20.0 mg, 0.058 mmol, 1.0 equiv.) and *trans*-crotonaldehyde (2.44 mg, 0.034 mmol, 0.6 equiv.). **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ: 6.87 ppm (m).

*B(2,4-$F_2H_3C_6O)_3$ (**4**):*

According to *General Procedure C*, using **4** (20.0 mg, 0.05 mmol, 1.0 equiv.) and *trans*-crotonaldehyde (2.1 mg, 0.03 mmol, 0.6 equiv.). **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ: Not determined.

*B(3,5-$F_2H_3C_6O)_3$ (**5**):*

According to *General Procedure C*, using **5** (20.0 mg, 0.05 mmol, 1.0 equiv.) and *trans*-crotonaldehyde (2.1 mg, 0.03 mmol, 0.6 equiv.). **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ: 6.87 ppm (m).

*B(2,3,4-$F_3H_2C_6O)_3$ (**6**):*

According to *General Procedure C*, using **6** (20.0 mg, 0.04 mmol, 1.0 equiv.) and *trans*-crotonaldehyde (1.86 mg, 0.03 mmol, 0.6 equiv.). **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ: 6.88 ppm (m).

*B(2,4,6-$F_3H_2C_6O)_3$ (**7**):*

According to *General Procedure C*, using **7** (20 mg, 0.04 mmol, 1.0 equiv.) and *trans*-crotonaldehyde (1.86 mg, 0.03 mmol, 0.6 equiv.). **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ: 6.88 ppm (m).

*B(3,4,5-$F_3H_2C_6O)_3$ (**8**):*

According to *General Procedure C*, using **8** (20.0 mg, 0.04 mmol, 1.0 equiv.) and *trans*-crotonaldehyde (1.86 mg, 0.03 mmol, 0.6 equiv.). **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ: 6.88 ppm (m).

5. NMR for the determination of Lewis acidity

Figure S33: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO without a Lewis acid present.

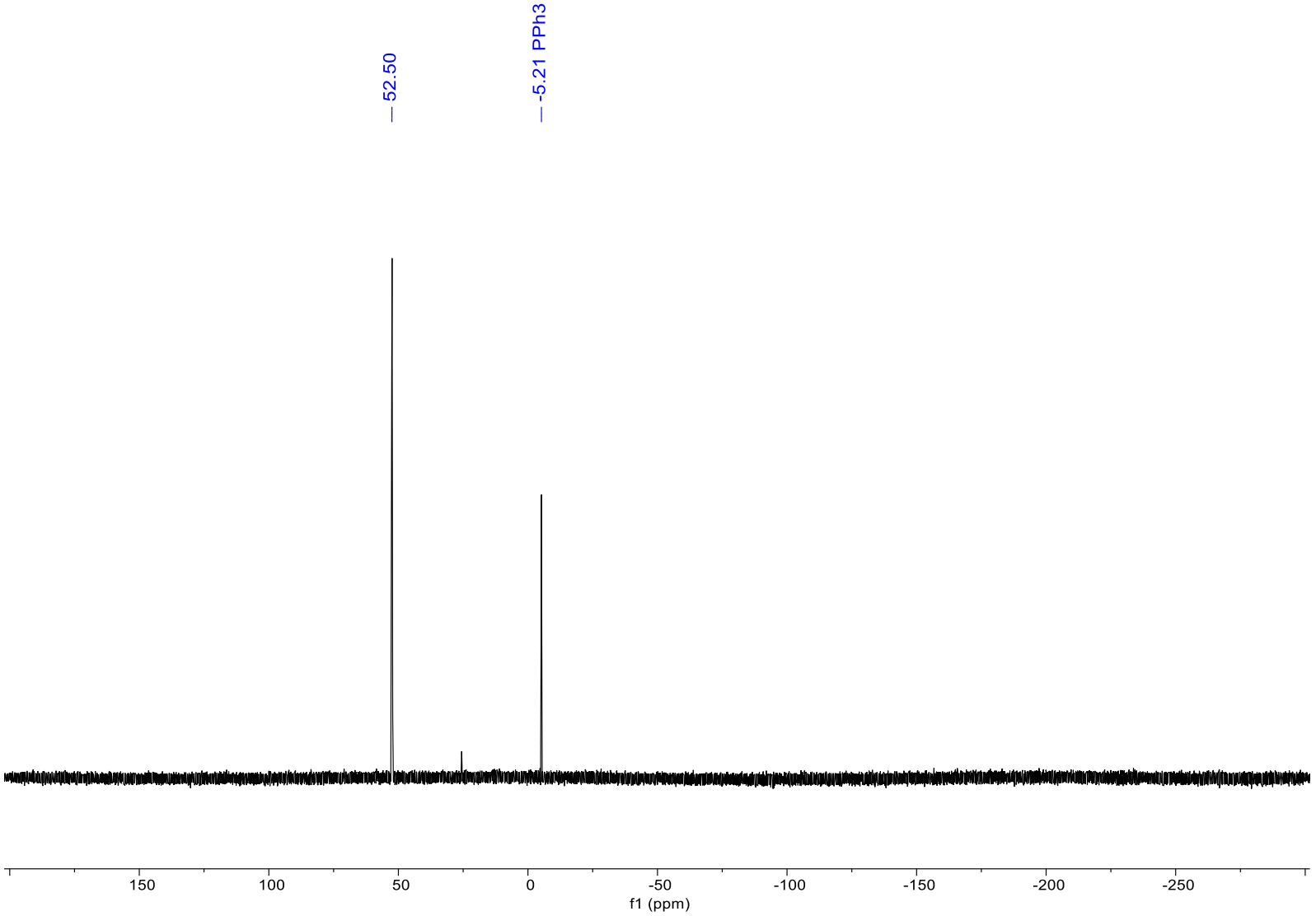


Figure S34: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO and $B(2\text{-}F_1H_4C_6O)_3$ (**1**).

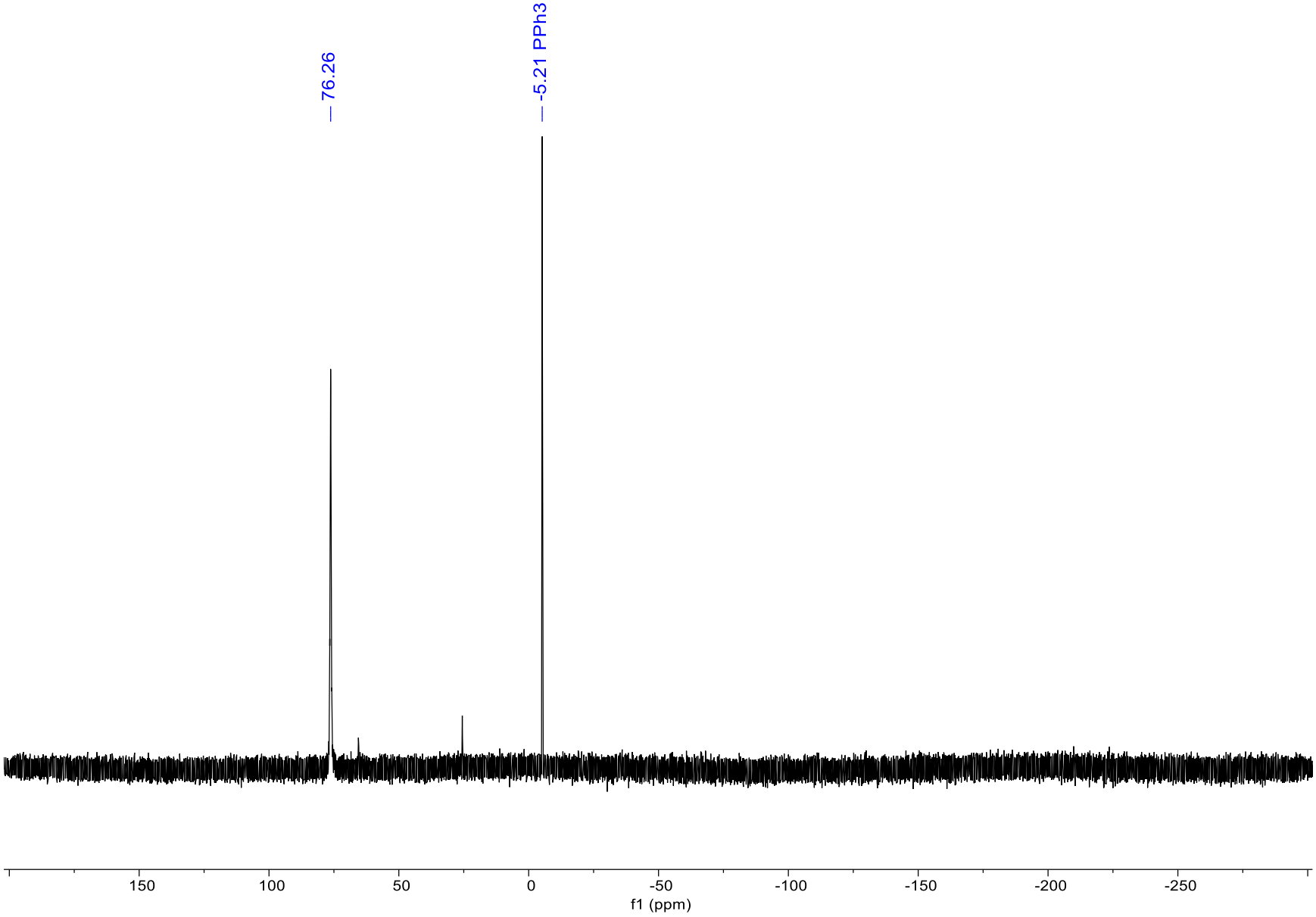


Figure S35: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO and $B(3\text{-}F_1H_4C_6O)_3$ (**2**).

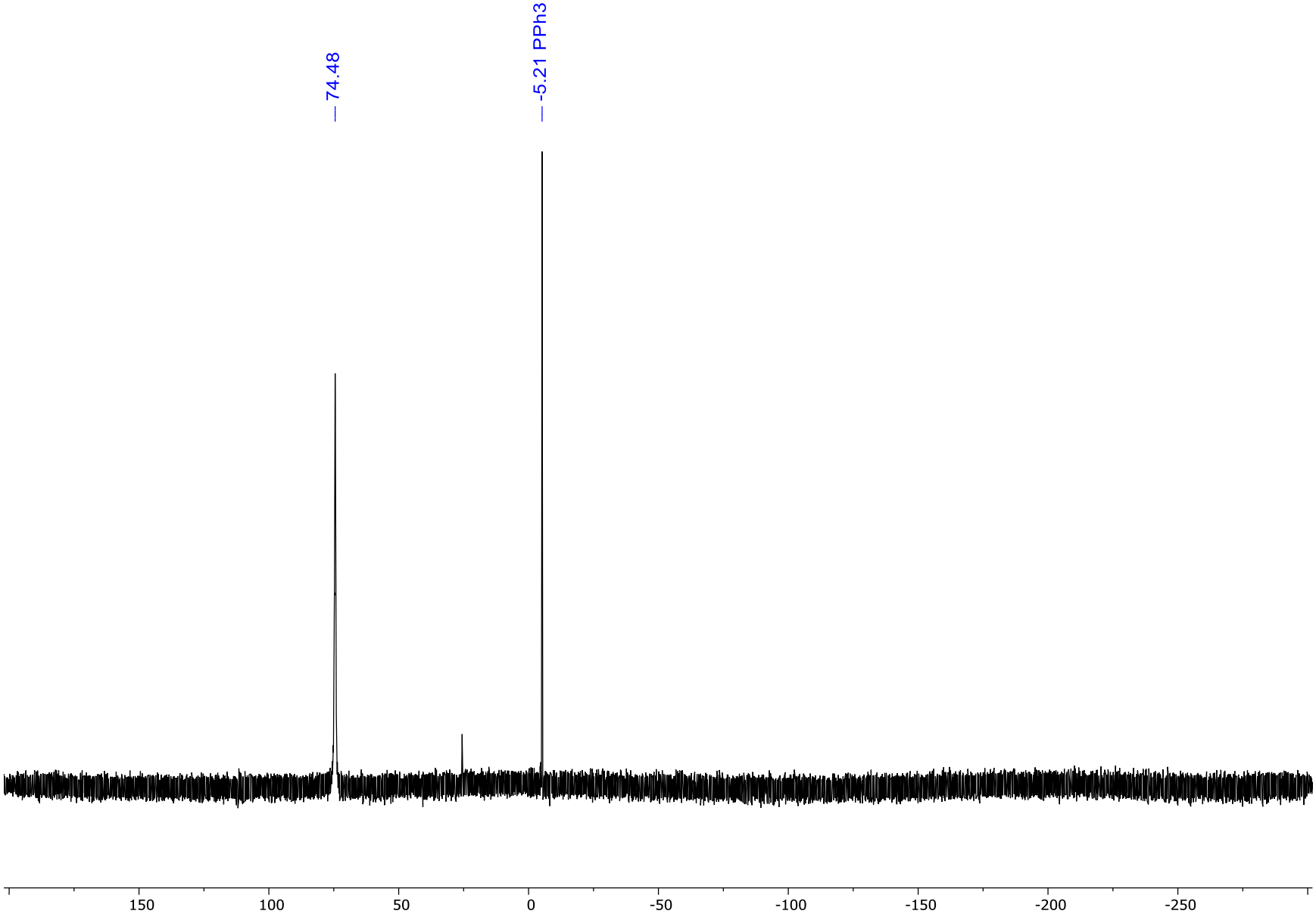


Figure S36: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO and $B(4\text{-}F_1H_4C_6O)_3$ (**3**).

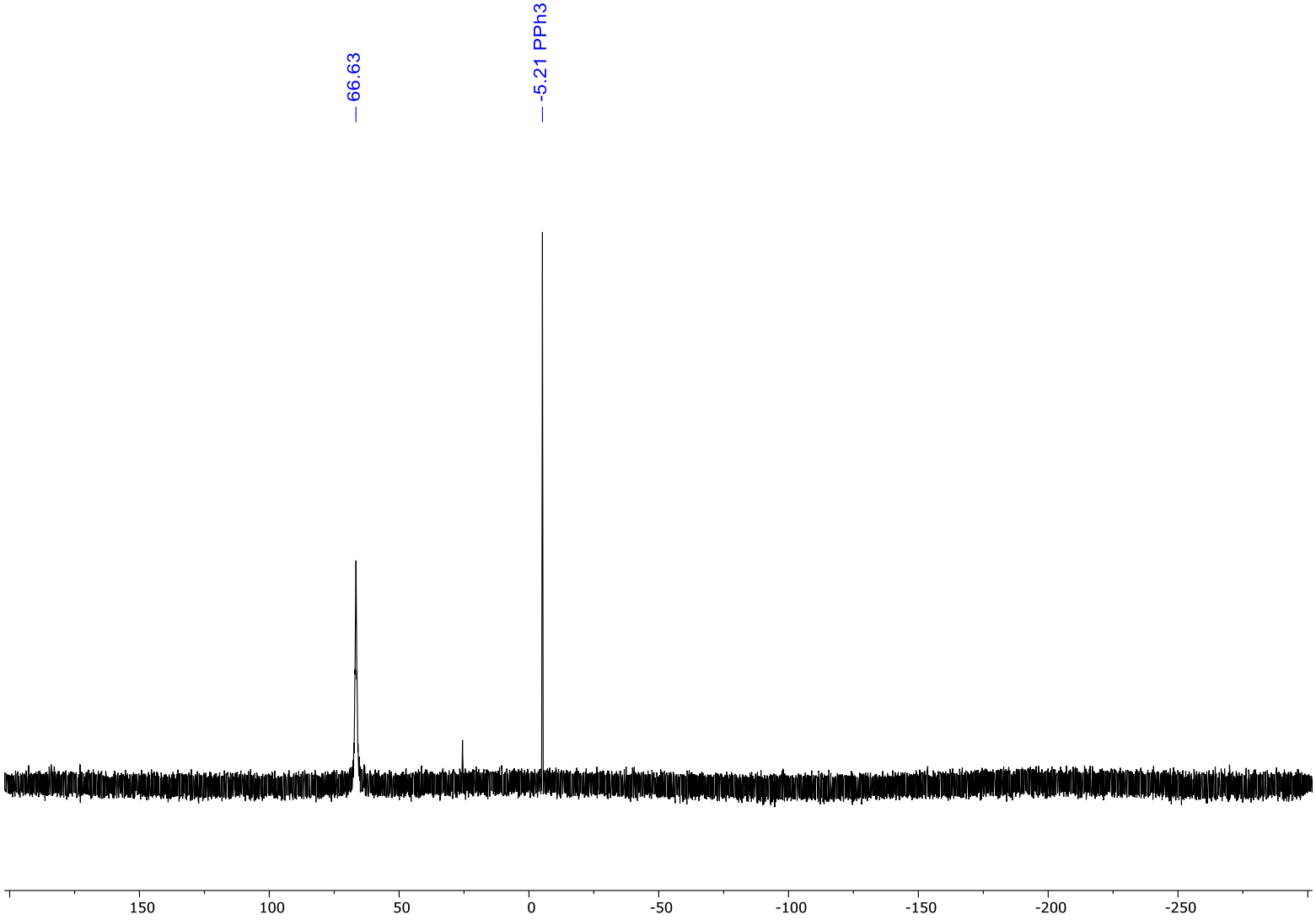


Figure S37: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO and $B(2,4\text{-}F_2H_3C_6O)_3$ (**4**).

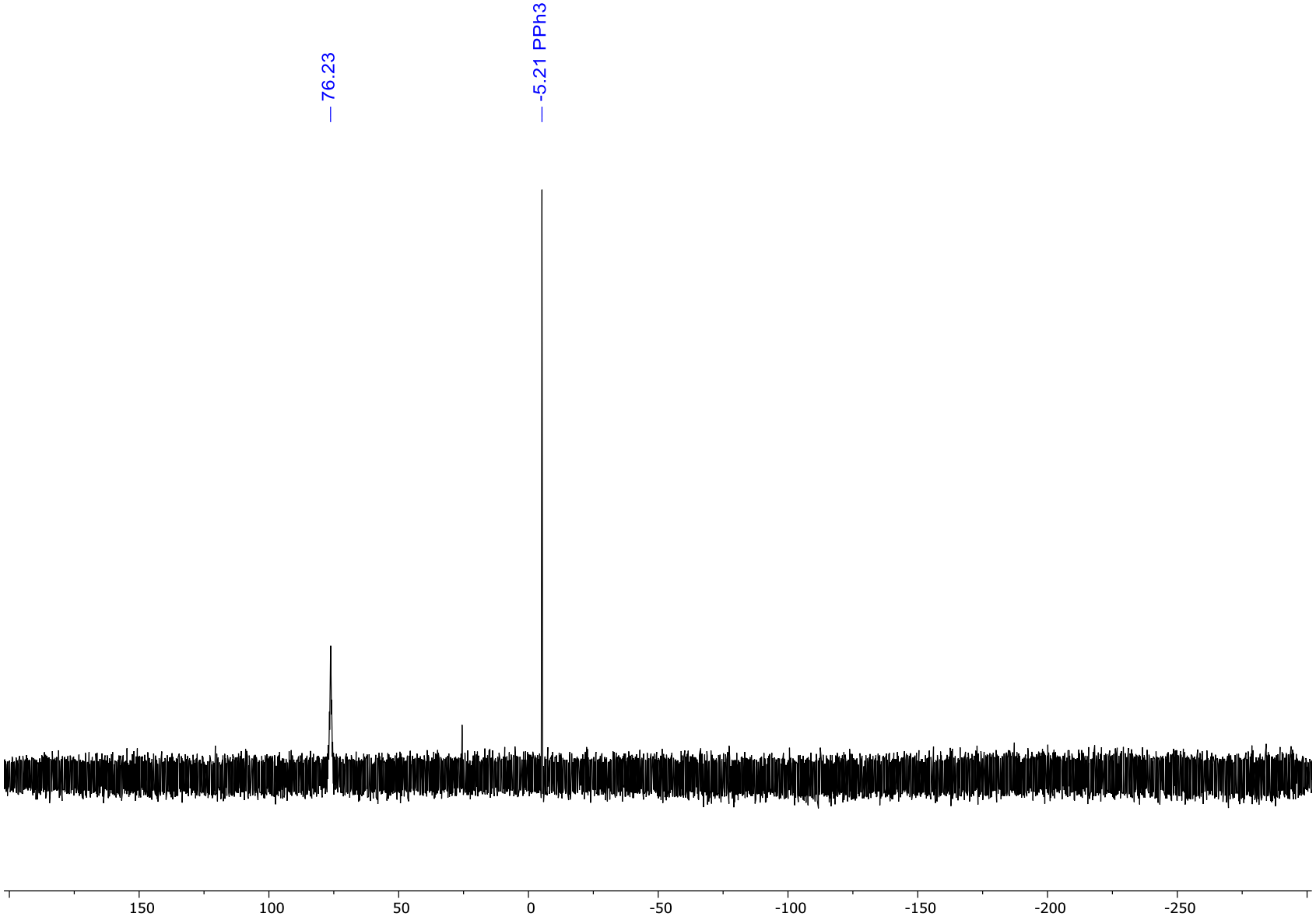


Figure S38: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO and $B(3,5\text{-}F_2H_3C_6O)_3$ (**5**).

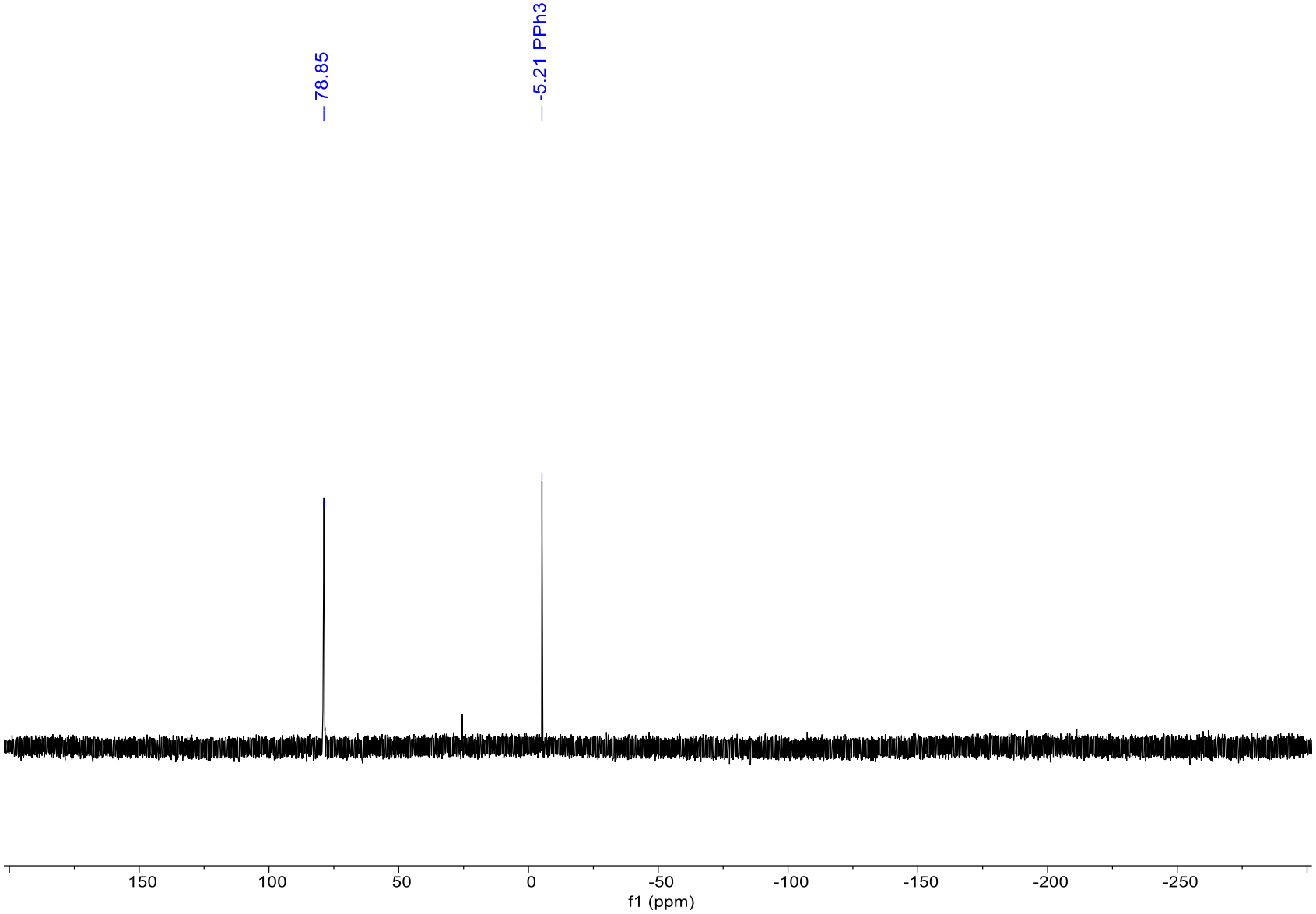


Figure S39: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO and $B(2,3,4\text{-}F_3H_2C_6O)_3$ (**6**).

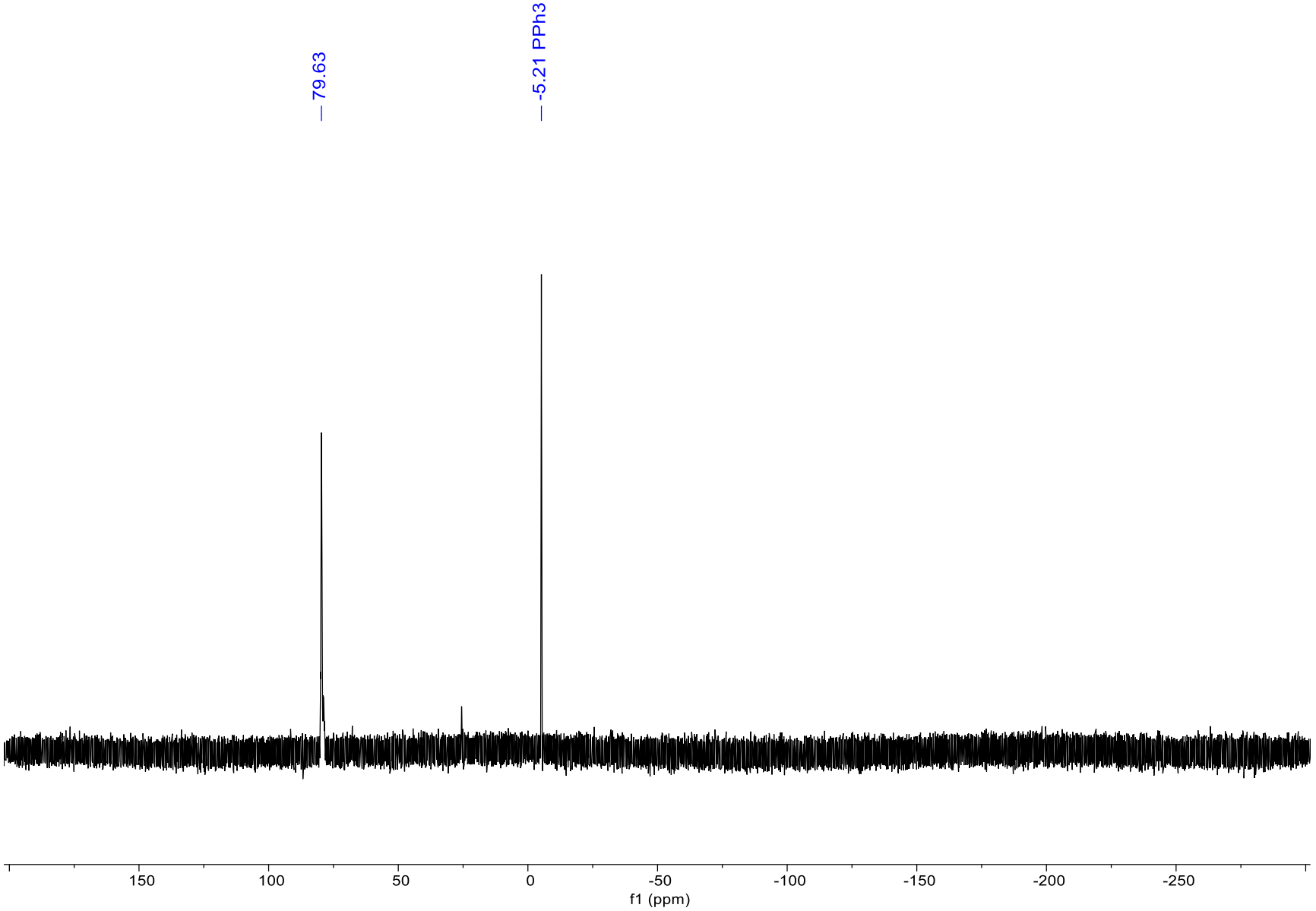


Figure S40: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO and $B(2,4,6\text{-}F_3H_2C_6O)_3$ (**7**).

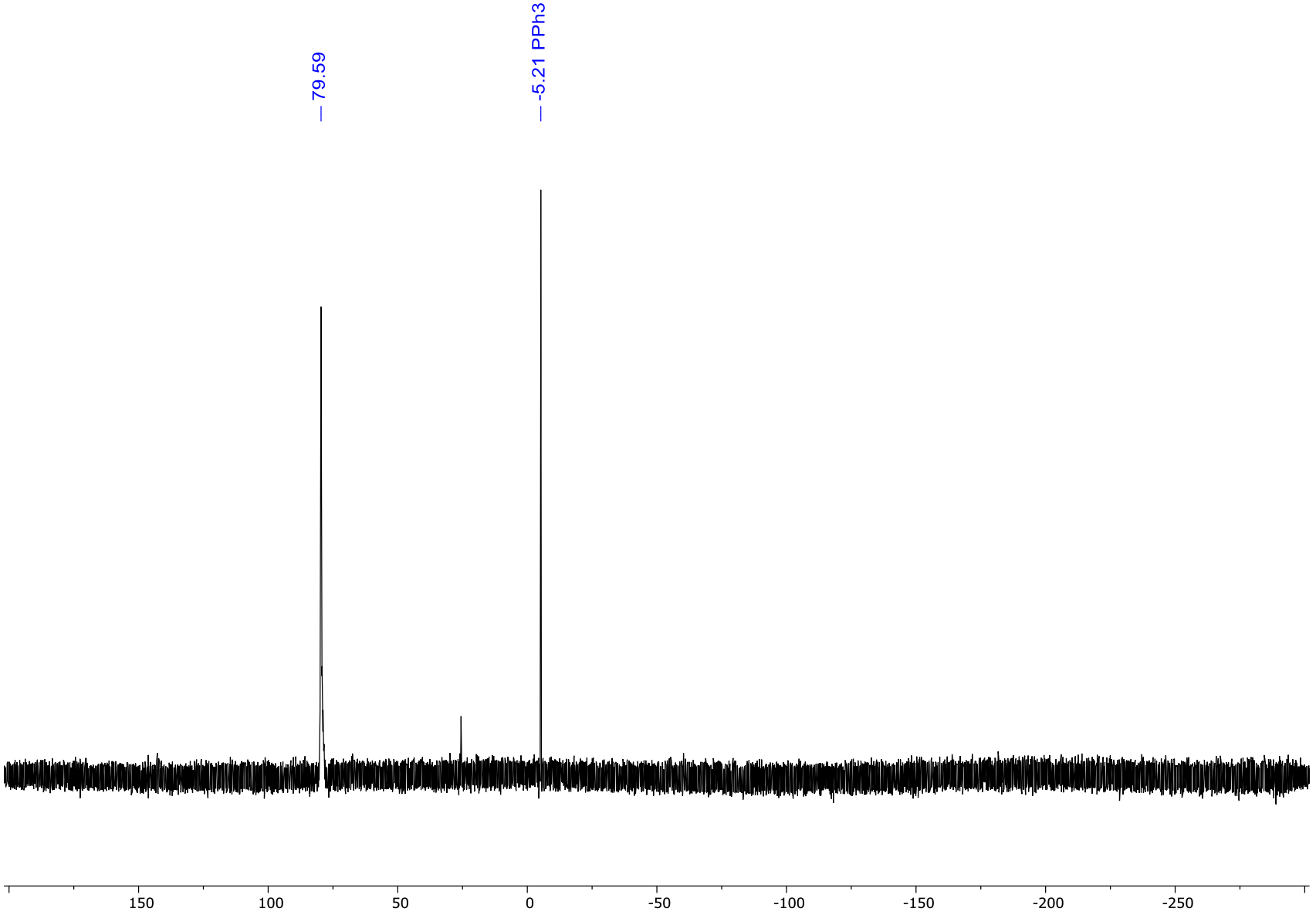


Figure S41: **^{31}P NMR** (202.5 MHz, $CDCl_3$) spectrum of Et_3PO and $B(3,4,5\text{-}F_3H_2C_6O)_3$ (**8**).

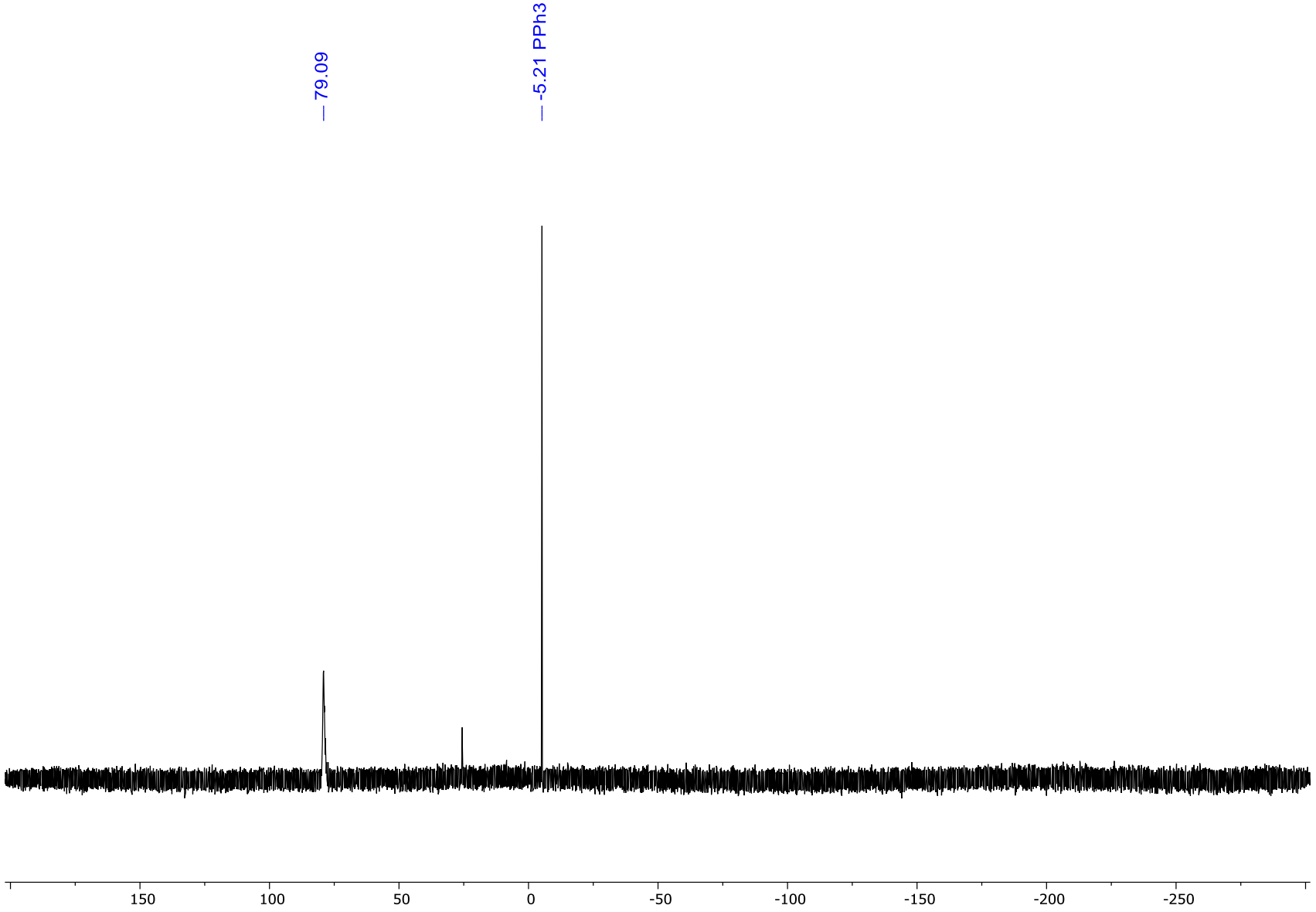


Figure S42: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde without a Lewis acid present.

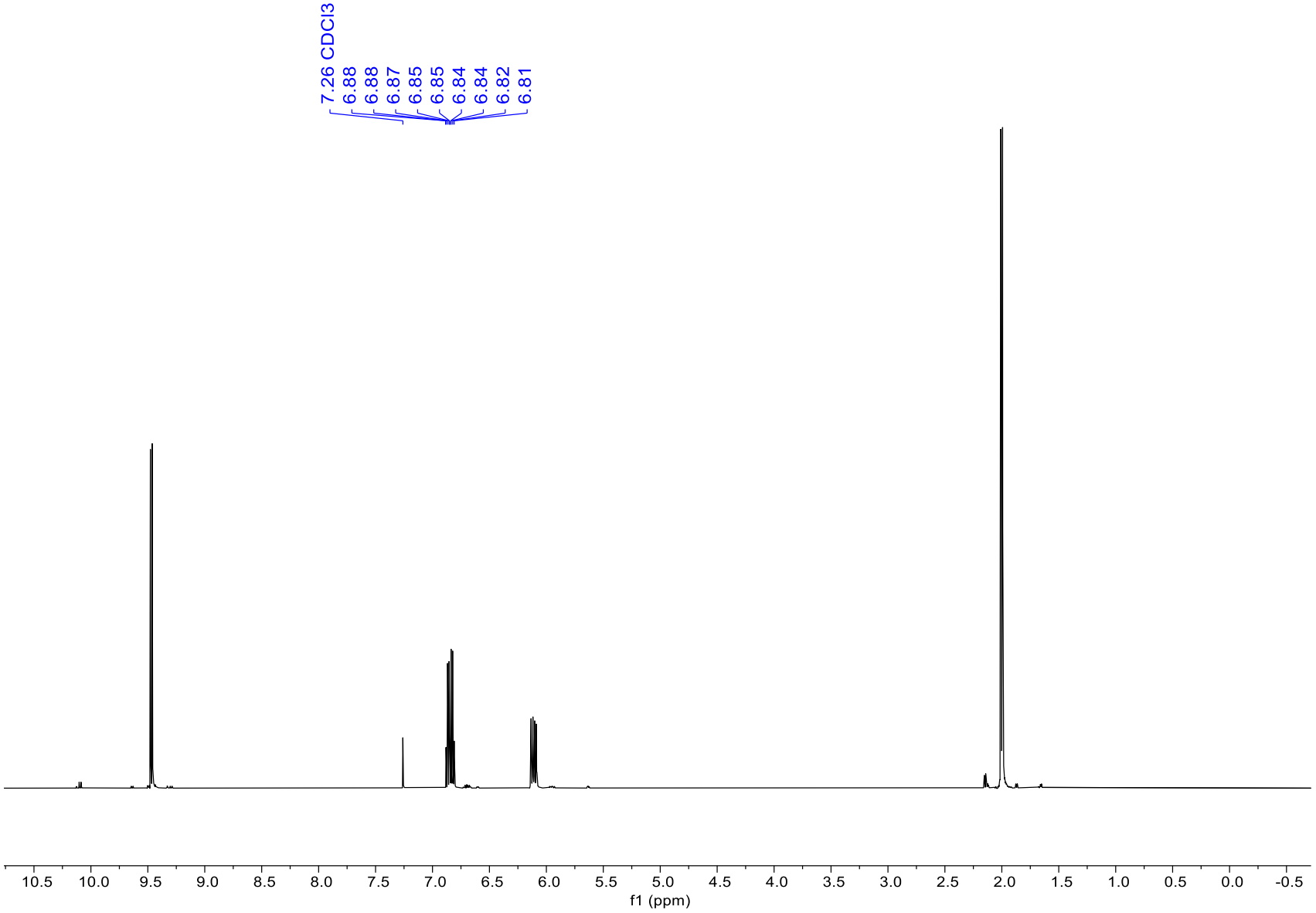


Figure S43: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde and $B(2\text{-}F_1H_4C_6O)_3$ (**1**).

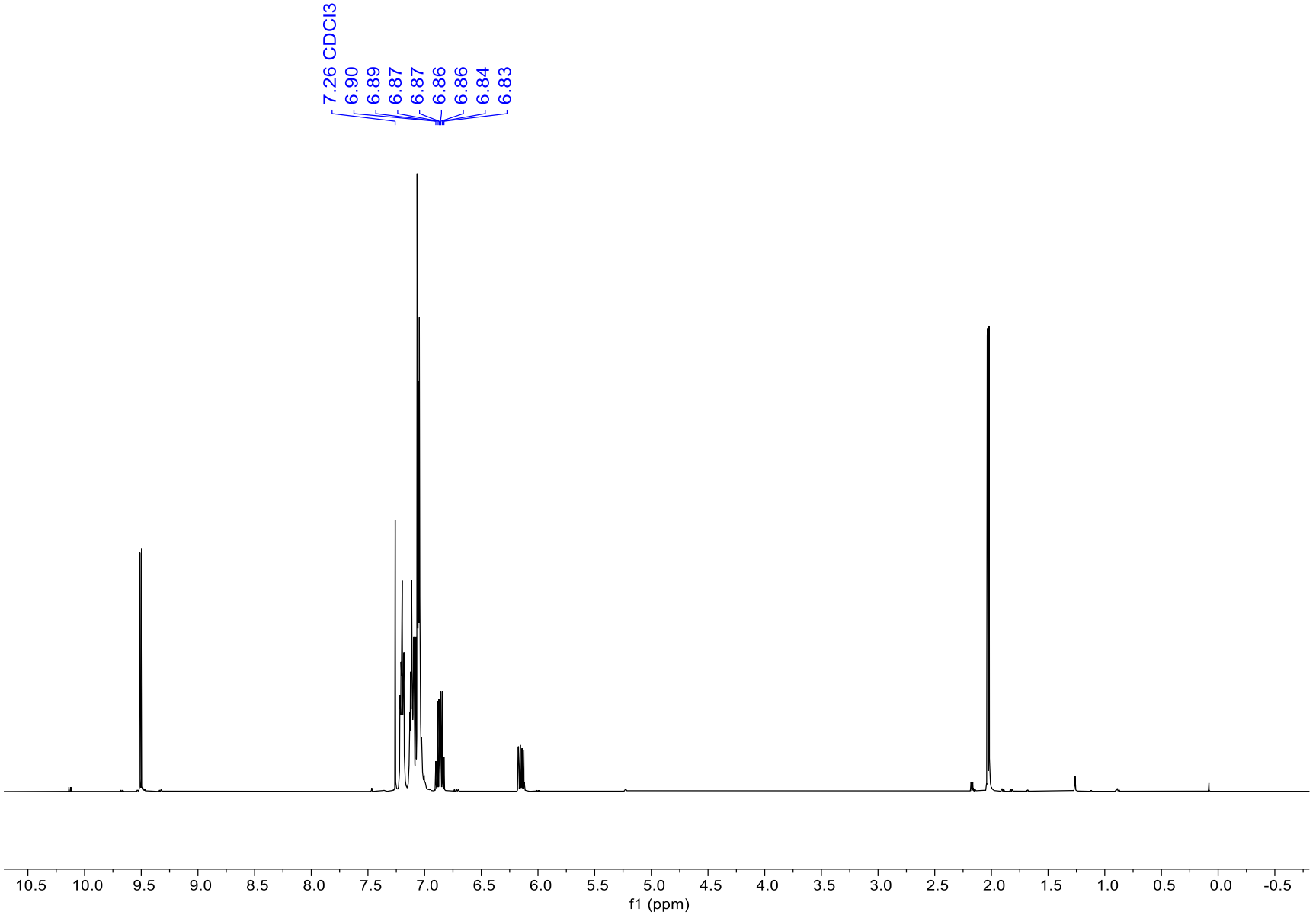


Figure S44: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde and $B(3\text{-}F_1H_4C_6O)_3$ (**2**).

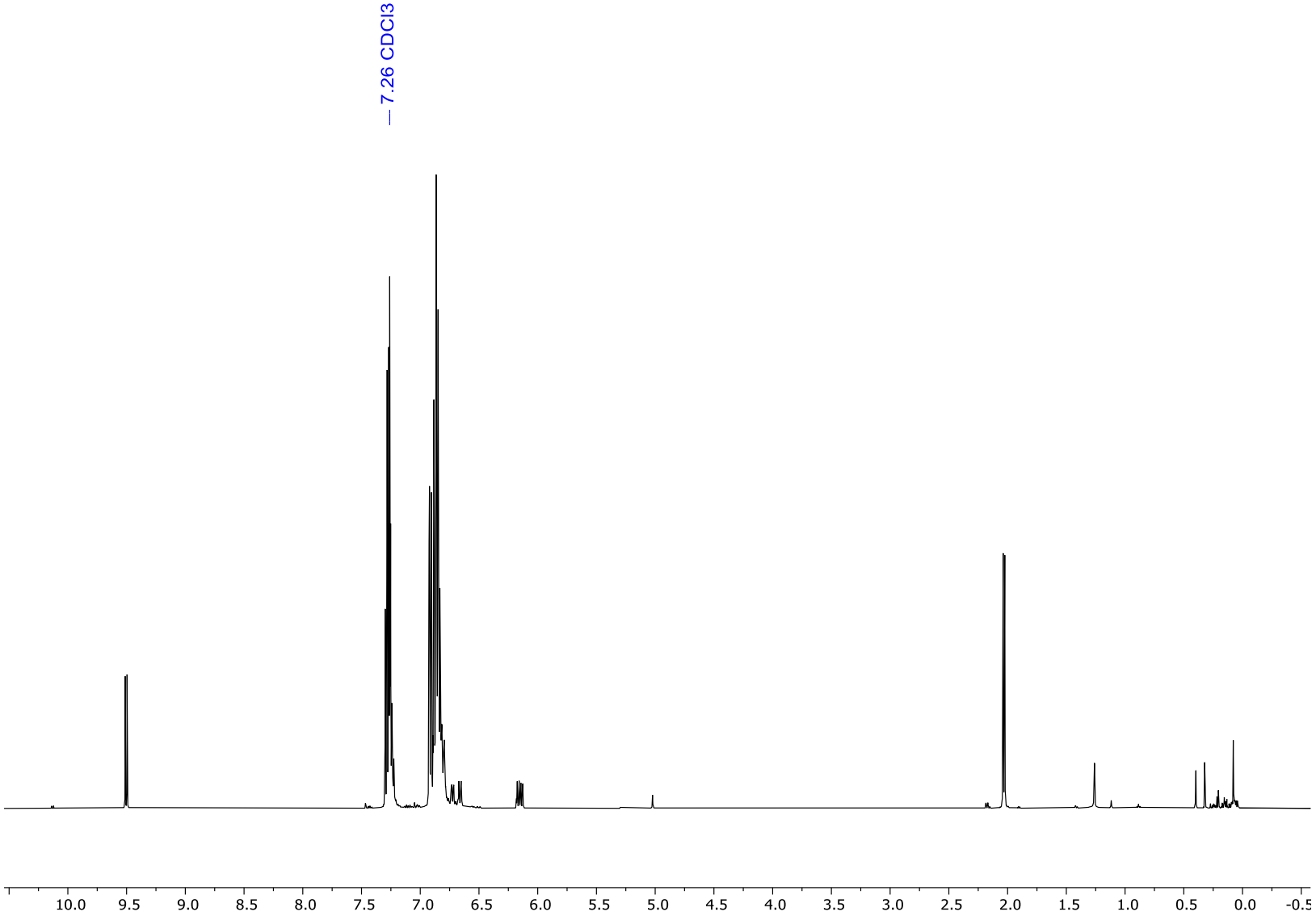


Figure S45: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde and $B(4\text{-}F_1H_4C_6O)_3$ (**3**).

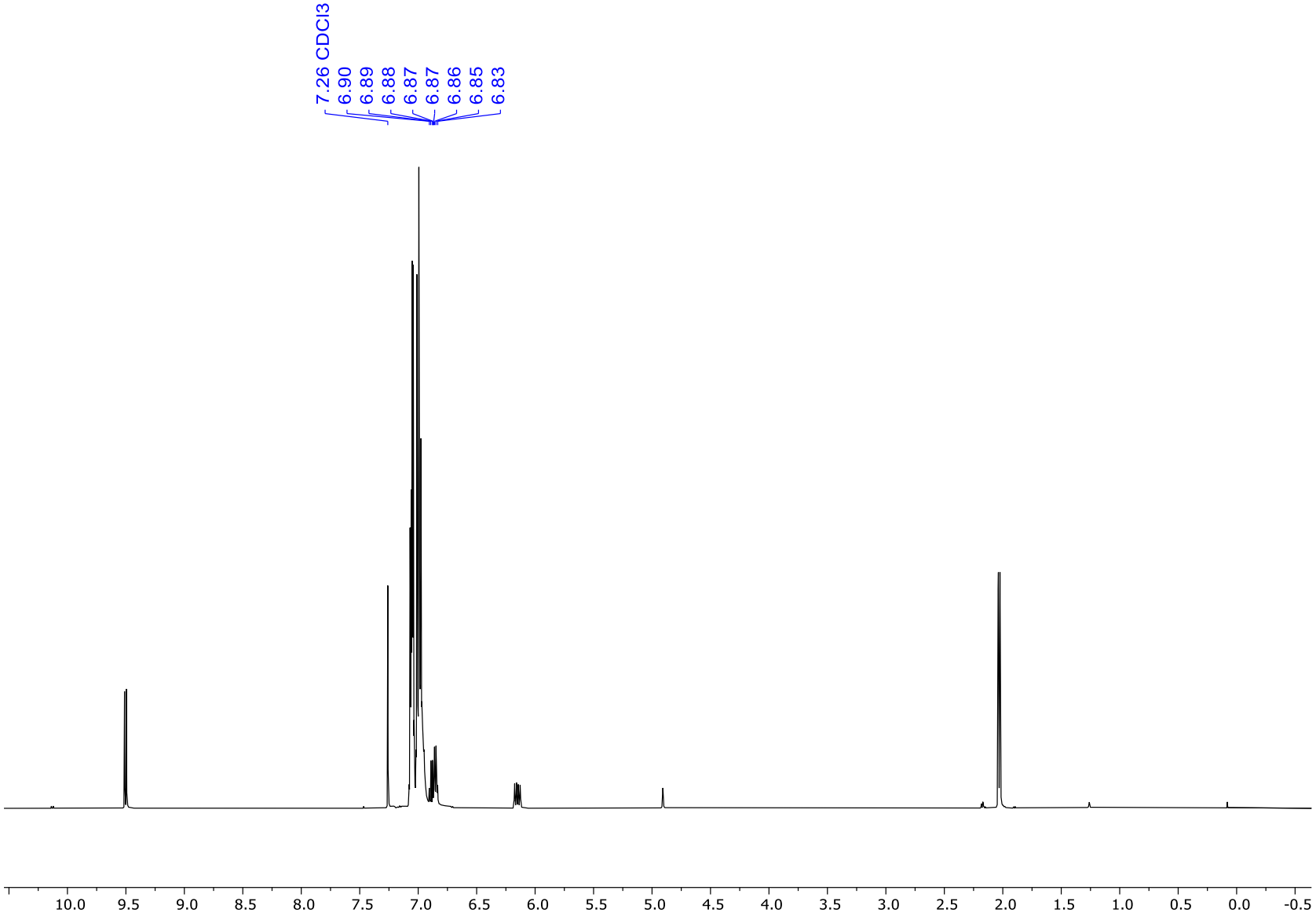


Figure S46: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde and B(2,4-$F_2H_3C_6O$) (**4**).

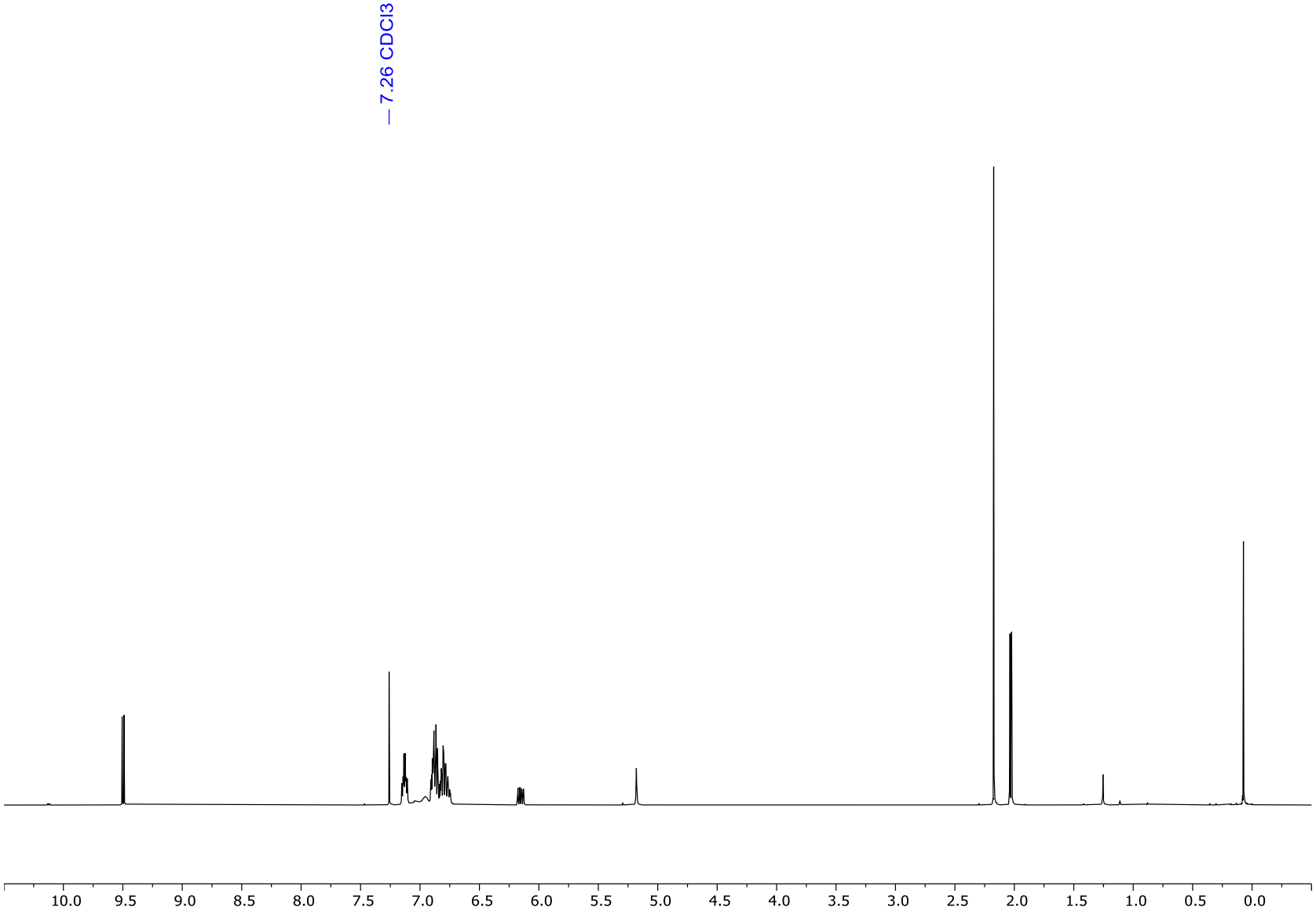


Figure S47: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde and $B(3,5\text{-}F_2H_3C_6O)_3$ (**5**).

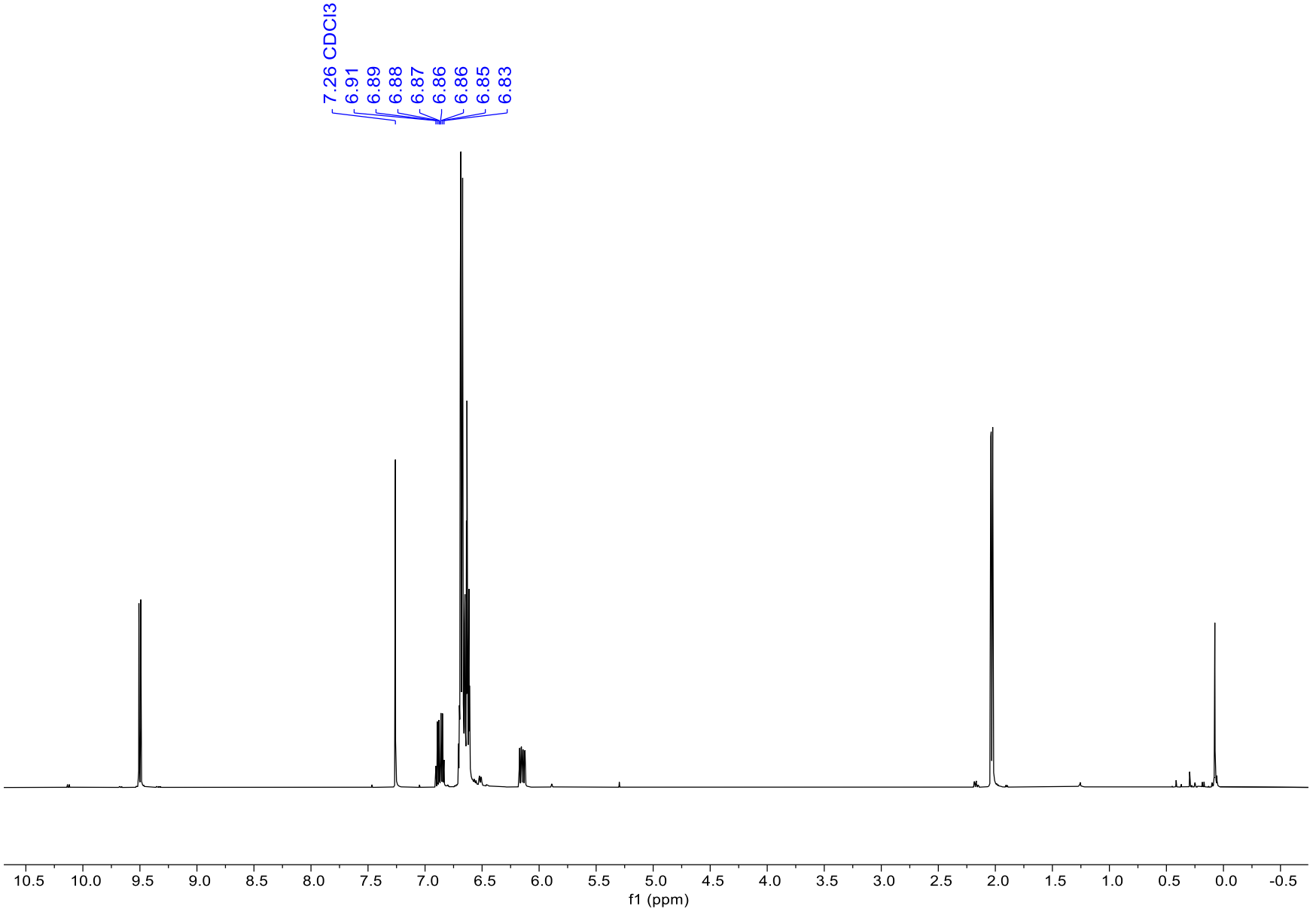


Figure S48: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde and B(2,3,4-$F_3H_2C_6O)_3$ (**6**).

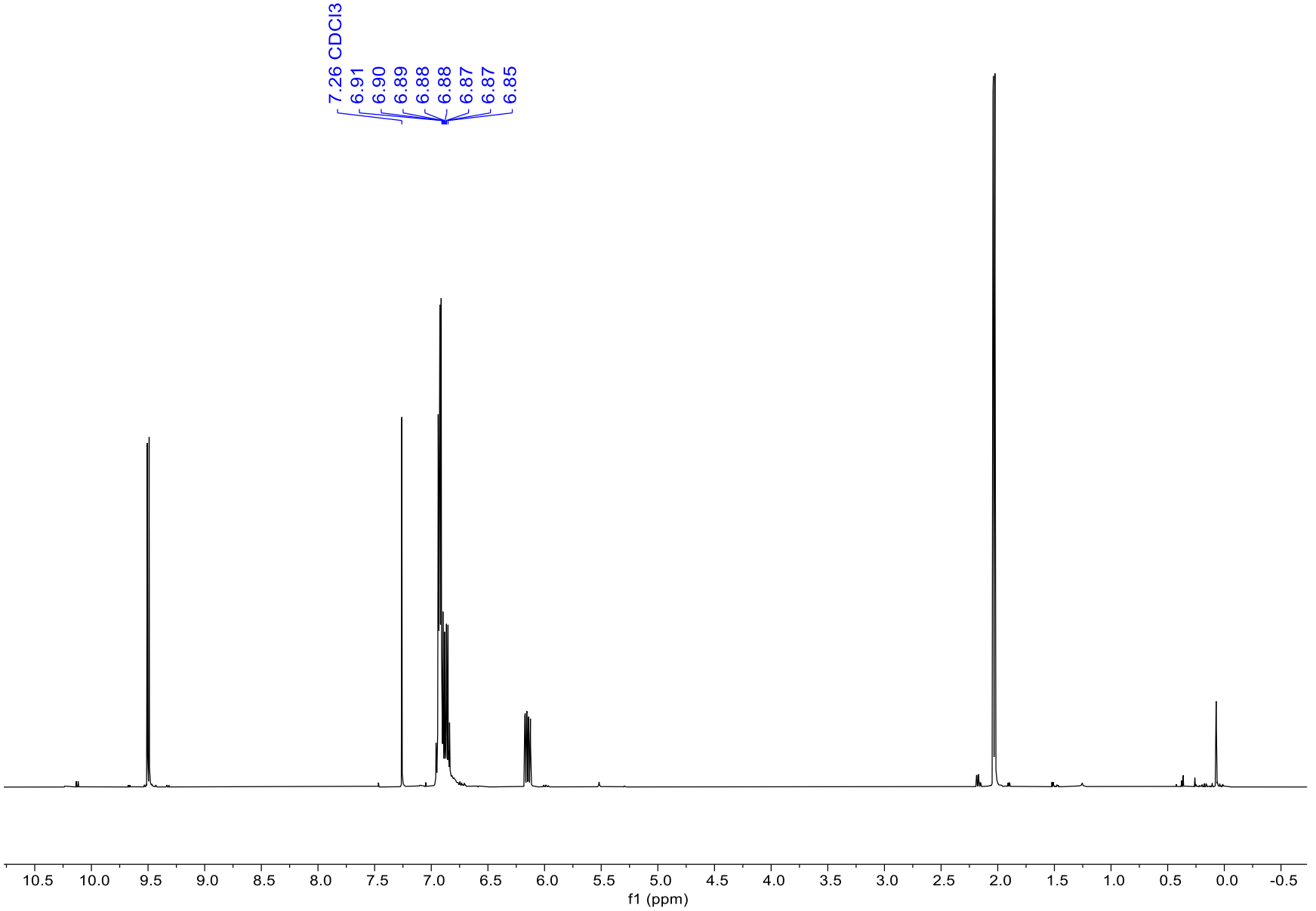


Figure S49: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde and B(2,4,6-$F_3H_2C_6O)_3$ (**7**).

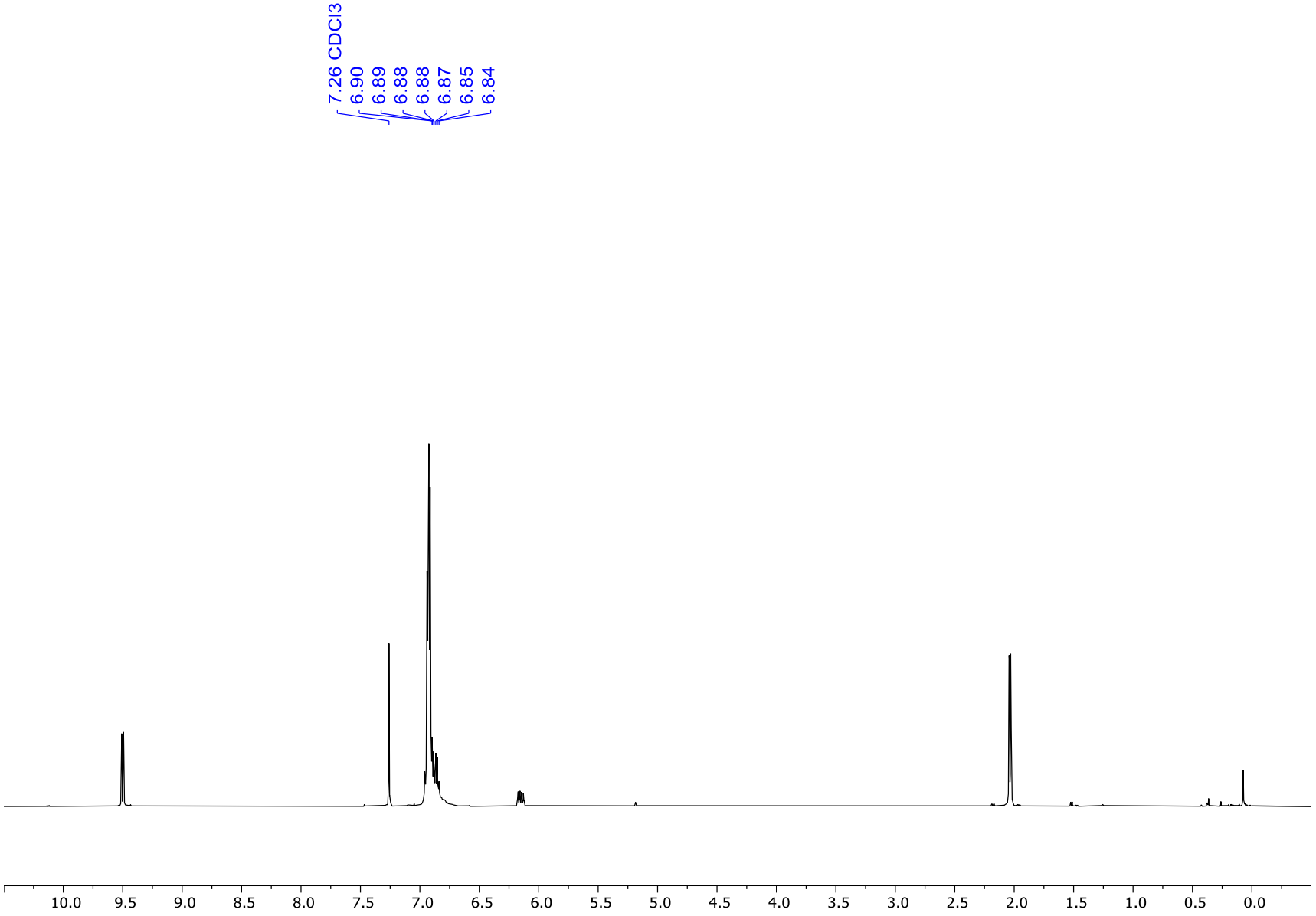
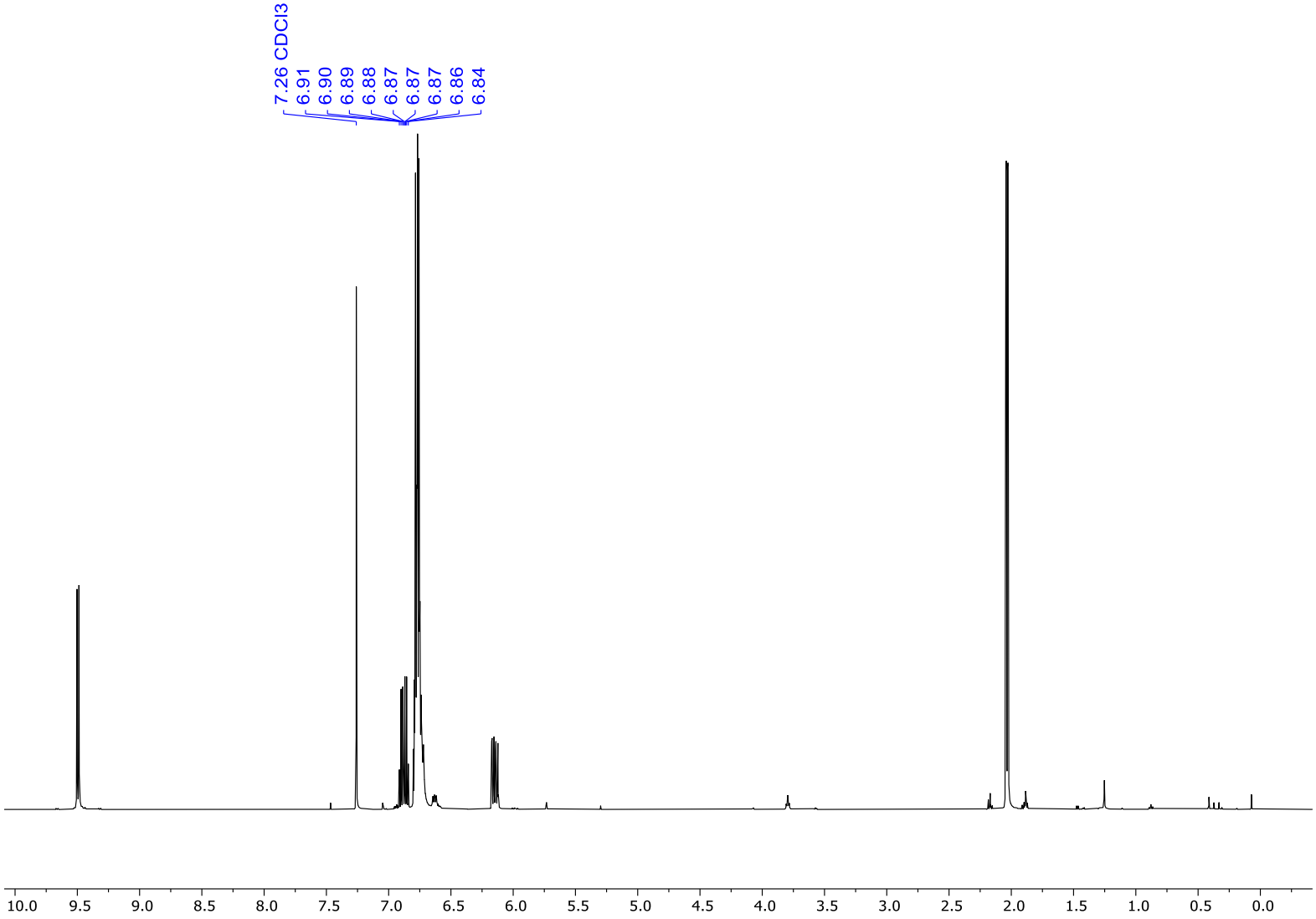


Figure S50: **^{1}H NMR** (500.2 MHz, $CDCl_3$) spectrum of *trans*-crotonaldehyde and B(3,4,5-$F_3H_2C_6O)_3$ (**8**).



6. Calculations

6.1 Computational details and geometry optimisation for XIA (X = F, H) calculations.

The borate starting geometries were optimised in Avogadro 1.2.0 with VSEPR UFF.[8] Geometry refinements were computed with PBEh-3c/def2-SVP executed in ORCA 5.0.3,[9] with *grid3*, *tightopt* and *verytightscf* settings.[10,11] Vibrational frequencies were determined to characterise the structure and verify they are energy minima. In the case of finding imaginary vibrations, the corresponding vibrational mode was plotted from the relevant *hess* file using the *orca_pltvib* tool, which is included in the orca distribution. The geometry was then displaced along the imaginary vibrational mode and used as a new input to re-optimise the structure. This process was repeated until no imaginary vibrations were obtained, and the structure was established to be at an energy minimum. Basis set superposition error (BSSE) for double hybrid functionals has previously been shown not to improve performance; hence all values are presented without BSSE correction.[12] We did not consider solvation models as previous literature showed linear correlations between the XIA_{vac} and XIA_{solv} (X = F, H) values, with consistently lower XIA_{solv} values than XIA_{vac}.[13]

6.2 Single point energies with M06-2X and isodesmic FIA/HIA determination

The single point electronic energies were calculated on the optimised geometries with M06-2X functional,[14] D3(zero) and def2-QZVPP basis set.[10,15] Resolution of identity and chain of spheres approximations were applied with *RIJCOSX* as default in ORCA 5.0.3.[16]

The *Thermal enthalpy correction* (2.47 kJ mol^{-1}) and *Total correction* of the energies were taken from the optimised geometries (PBEh-3c) and added to the *Final single point energy* (M06-2X) for the Lewis acid and the X (X = F, H) ion adduct. The XIA (X = F, H) values were anchored to an appropriate reference system using equations 1a to 2c (see below). The FIA of the COF_2/COF_3^- reference system has previously been experimentally determined (208.8 kJ mol^{-1}) and successfully utilised as a benchmark for these calculations. The tetramethylsilane (TMS) system could be used as the benchmark for FIA values; however, Greb's 2020 paper showed that COF_2 was more appropriate for the M06 level of theory.[17] For the HIA benchmark, the Me_3SiH/Me_3Si^+ reference system was considered, for which enthalpy (924 kJ mol^{-1}) has previously been established from high accuracy coupled-cluster computational methods, CCSD(T).[12] These methods enable the determination of XIA values with an accuracy of ±5 kJ mol^{-1}.[17]

(Eqn. 1a) $[\mathbf{B}] + COF_3^- \xrightarrow{\Delta H_{computed}} [\mathbf{B}\text{-}F]^- + COF_2$

(Eqn. 1b) $COF_3^- \xrightarrow[= 208.8\ kJ\ mol^{-1}]{\Delta H_{benchmark}} COF_2 + F^-$

(Eqn. 1c) $FIA = \Delta H_{computed} - \Delta H_{benchmark}$

(Eqn. 2a) $[\mathbf{B}] + Me_3SiH \xrightarrow{\Delta H_{computed}} [\mathbf{B}\text{-}H]^- + Me_3Si^+$

(Eqn. 2b) $Me_3SiH \xrightarrow[= 924\ kJ\ mol^{-1}]{\Delta H_{benchmark}} Me_3Si^+ + H^-$

(Eqn. 2c) $HIA = \Delta H_{computed} - \Delta H_{benchmark}$

Where [**B**] is a boron Lewis acid.

Table S3. Calculated anchored FIA values from energy values of [Complex] and [F-Complex].

	Electronic Energy (Ha)	Total Correction (Ha)	Thermal Enthalpy Correction (Ha)	Total E (Ha)	Electronic Energy (Ha)	Total Correction (Ha)	Thermal Enthalpy Correction (Ha)	Total E (Ha)	Anchored FIA (Ha)	Anchored FIA (kJ mol^{-1})
FIA	**[Complex]**				**[F-Complex]**					
Reference System										
COF_2	-313.07133	0.01812	0.00094	-313.05227	-412.85436	0.02105	0.00094	-412.83236		
Boron Lewis Acids										
$B(C_6F_5)_3$	-2208.62819	0.18926	0.00094	-2208.43799	-2308.66375	0.19192	0.00094	-2308.47089	-0.25280	454.92561
$B(OPh)_3$	-945.67268	0.31760	0.00094	-945.35414	-1045.66757	0.31947	0.00094	-1045.34716	-0.21293	350.24841
$B(OC_6F_5)_3$	-2434.43357	0.20712	0.00094	-2434.22550	-2534.45924	0.20879	0.00094	-2534.24951	-0.24391	431.58508
$B(O(2\text{-}FC_6H_4))_3$ [**1**]	-1243.44263	0.29521	0.00094	-1243.14647	-1343.43794	0.29705	0.00094	-1343.13995	-0.21338	351.42621
$B(O(3\text{-}FC_6H_4))_3$ [**2**]	-1243.45194	0.29511	0.00094	-1243.15588	-1343.45393	0.29699	0.00094	-1343.15599	-0.22002	368.85754
$B(O(4\text{-}FC_6H_4))_3$ [**3**]	-1243.44859	0.29510	0.00094	-1243.15255	-1343.44702	0.29705	0.00094	-1343.14902	-0.21637	359.29145
$B(O(2,4\text{-}F_2C_6H_3))_3$ [**4**]	-1541.21264	0.27272	0.00094	-1540.93897	-1641.21785	0.27491	0.00094	-1640.94200	-0.22293	376.49039
$B(O(3,5\text{-}F_2C_6H_3))_3$ [**5**]	-1541.22619	0.27269	0.00094	-1540.95256	-1641.24196	0.27481	0.00094	-1640.96621	-0.23356	404.39888
$B(O(2,3,4\text{-}F_3C_6H_2))_3$ [**6**]	-1838.95347	0.25099	0.00094	-1838.70153	-1938.96834	0.25309	0.00094	-1938.71430	-0.23267	402.08812
$B(O(2,4,6\text{-}F_3C_6H_2))_3$ [**7**]	-1838.97441	0.25071	0.00094	-1838.72276	-1938.97787	0.25255	0.00094	-1938.72438	-0.22153	372.82018
$B(O(3,4,5\text{-}F_3C_6H_2))_3$ [**8**]	-1838.95948	0.25066	0.00094	-1838.70787	-1938.98816	0.25305	0.00094	-1938.73417	-0.24620	437.59998

Table S4. Calculated anchored HIA values from energy values of [Complex] and [F-Complex].

	Electronic Energy (Ha)	Total Correction (Ha)	Thermal Enthalpy Correction (Ha)	Total E (Ha)	Electronic Energy (Ha)	Total Correction (Ha)	Thermal Enthalpy Correction (Ha)	Total E (Ha)	Anchored HIA (Ha)	Anchored HIA (kJ mol-1)
HIA	**[Complex]**				**[H-Complex]**					
Reference System										
Me_3Si	-408.96665	0.11717	0.00094	-408.84854	-409.84916	0.12992	0.00094	-409.71830		
Boron Lewis Acids										
$B(C_6F_5)_3$	-2208.62819	0.18926	0.00094	-2208.43799	-2209.34431	0.19807	0.00094	-2209.14530	0.16245	497.47861
$B(OPh)_3$	-945.67268	0.31760	0.00094	-945.35414	-946.32129	0.32508	0.00094	-945.99526	0.22863	323.73056
$B(OC_6F_5)_3$	-2434.43357	0.20712	0.00094	-2434.22550	-2435.11564	0.21453	0.00094	-2434.90016	0.19510	411.76647
$B(O(2\text{-}FC_6H_4))_3$ [**1**]	-1243.44263	0.29521	0.00094	-1243.14647	-1244.09762	0.30293	0.00094	-1243.79374	0.22249	339.85642
$B(O(3\text{-}FC_6H_4))_3$ [**2**]	-1243.45194	0.29511	0.00094	-1243.15588	-1244.10689	0.30269	0.00094	-1243.80326	0.22238	340.14286
$B(O(4\text{-}FC_6H_4))_3$ [**3**]	-1243.44859	0.29510	0.00094	-1243.15255	-1244.09937	0.30271	0.00094	-1243.79572	0.22660	329.07478
$B(O(2,4\text{-}F_2C_6H_3))_3$ [**4**]	-1541.21264	0.27272	0.00094	-1540.93897	-1541.87565	0.28073	0.00094	-1541.59398	0.20828	377.16235
$B(O(3,5\text{-}F_2C_6H_3))_3$ [**5**]	-1541.22619	0.27269	0.00094	-1540.95256	-1541.89553	0.28054	0.00094	-1541.61404	0.20828	377.16235
$B(O(2,3,4\text{-}F_3C_6H_2))_3$ [**6**]	-1838.95347	0.25099	0.00094	-1838.70153	-1839.62182	0.25877	0.00094	-1839.36211	0.20918	374.79085
$B(O(2,4,6\text{-}F_3C_6H_2))_3$ [**7**]	-1838.97441	0.25071	0.00094	-1838.72276	-1839.63205	0.25825	0.00094	-1839.37285	0.21966	347.28712
$B(O(3,4,5\text{-}F_3C_6H_2))_3$ [**8**]	-1838.95948	0.25066	0.00094	-1838.70787	-1839.64311	0.25874	0.00094	-1839.38342	0.19421	414.10357

6.3 Computational details and geometry optimisation for GEI determination

All calculations were performed with ORCA 5.0.3. Starting VSEPR geometries were optimised in Avogadro 1.2.0 with UFF.[9] Geometry optimisations were calculated at the B3LYP/def2-TZVP level of theory as executed in ORCA, with the application of *grid3*, *tightopt* and *verytightscf* settings.[18,19] Vibrational frequencies were determined to verify the calculated geometries were at an energy minima through the absence of any imaginary frequencies.

The GEI values (ω) were calculated using Eqn 3a below, based on the Mulliken electronegativity (χ) (Eqn 3b) and chemical hardness (η) (Eqn 3c). The input variables E_{HOMO} and E_{LUMO} were taken as the Kohn-Sham orbitals in eV.

Eqn. 3a $$\omega[\mathbf{B}] = \chi[\mathbf{B}]^2 / 2\eta[\mathbf{B}]$$

Eqn. 3b $$\chi[\mathbf{B}] = -^1/_2 (E_{HOMO}[\mathbf{B}] + E_{LUMO}[\mathbf{B}])$$

Eqn. 3c $$\eta[\mathbf{B}] = (E_{LUMO}[\mathbf{B}] - E_{HOMO}[\mathbf{B}])$$

Where [**B**] is a boron Lewis acid.

The use of a solvation model was not considered, as a previous literature report has shown linear correlations between the GEI_{vac} and GEI_{solv} values, with consistent lower GEI_{solv} values than GEI_{vac}, as seen for XIA (X = H, F) values too.[13]

Table S5. Calculated GEI values from HOMO, LUMO, Mulliken and Hardness values.

	LUMO (eV)	HOMO (eV)	-1/2[HOMO+LUMO] (eV)	LUMO-HOMO (eV)	Mulliken^2/2Hardness (eV)
GEI			**Mulliken (χ)**	**Hardness (η)**	**GEI (ω)**
Boron Lewis Acids					
$B(C_6F_5)_3$	-3.4296	-7.5599	-5.49475	4.1303	3.65497392
$B(OPh)_3$	-0.3906	-6.4795	-3.43505	6.0889	0.968940901
$B(OC_6F_5)_3$	-1.2694	-7.5069	-4.38815	6.2375	1.543555946
$B(O(2\text{-}FC_6H_4))_3$ [**1**]	-0.7532	-6.4424	-3.5978	5.6892	1.137608525
$B(O(3\text{-}FC_6H_4))_3$ [**2**]	-0.7551	-6.7231	-3.7391	5.968	1.171319438
$B(O(4\text{-}FC_6H_4))_3$ [**3**]	-0.8576	-6.5714	-3.7145	5.7138	1.207384775
$B(O(2,4\text{-}F_2C_6H_3))_3$ [**4**]	-1.1709	-6.5553	-3.8631	5.3844	1.385812868
$B(O(3,5\text{-}F_2C_6H_3))_3$ [**5**]	-0.9084	-7.1446	-4.0265	6.2362	1.299886329
$B(O(2,3,4\text{-}F_3C_6H_2))_3$ [**6**]	-0.9223	-7.0306	-3.97645	6.1083	1.294317126
$B(O(2,4,6\text{-}F_3C_6H_2))_3$ [**7**]	-1.0959	-6.8159	-3.9559	5.72	1.367932239
$B(O(3,4,5\text{-}F_3C_6H_2))_3$ [**8**]	-1.0745	-7.1175	-4.096	6.043	1.388152904
	LUMO+1 (eV)	**HOMO (eV)**	**-1/2[HOMO+LUMO]**	**LUMO-HOMO**	**Mulliken^2/2Hardness**
			Mulliken (χ)	**Hardness (η)**	**GEI (ω)**
$B(OPh)_3$	-0.3713	-6.4795	-3.4254	7.1886	0.816109198
$B(OC_6F_5)_3$	-1.2228	-7.5069	-4.36485	5.2567	1.812155489
$B(O(2\text{-}FC_6H_4))_3$ [**1**]	-0.5413	-6.4424	-3.49185	6.9656	0.875230879
$B(O(3\text{-}FC_6H_4))_3$ [**2**]	-0.6839	-6.7231	-3.7035	5.7585	1.19092752
$B(O(4\text{-}FC_6H_4))_3$ [**3**]	-0.6839	-6.5714	-3.62765	6.0392	1.089535412
$B(O(2,4\text{-}F_2C_6H_3))_3$ [**4**]	-0.9312	-6.5553	-3.74325	5.6402	1.242147491
$B(O(3,5\text{-}F_2C_6H_3))_3$ [**5**]	-0.7001	-7.1446	-3.92235	5.8552	1.313774894
$B(O(2,3,4\text{-}F_3C_6H_2))_3$ [**6**]	-0.9743	-7.0306	-4.00245	6.1703	1.298122134
$B(O(2,4,6\text{-}F_3C_6H_2))_3$ [**7**]	-0.9218	-6.8159	-3.86885	6.1088	1.225117889
$B(O(3,4,5\text{-}F_3C_6H_2))_3$ [**8**]	-1.0644	-7.1175	-4.09095	5.7515	1.454913666

6.4 Visual representation of computed orbitals

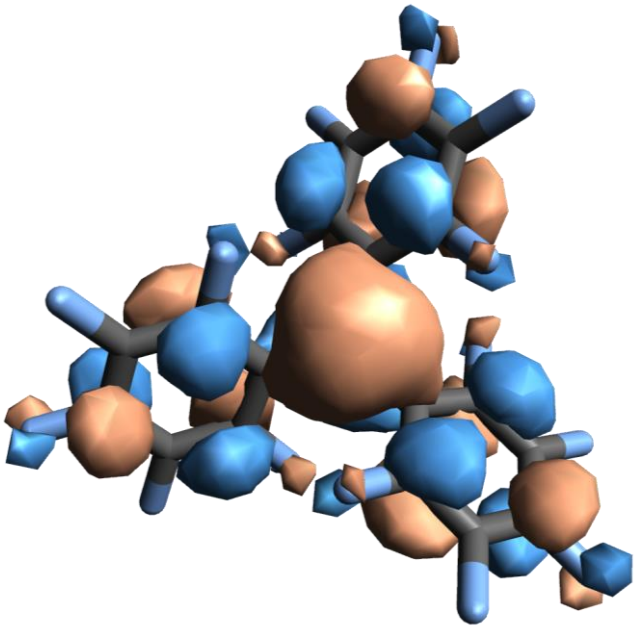


Figure S52. Top view representation of LUMO of $B(C_6F_5)_3$ at B3LYP/def2-TZVP level of theory.

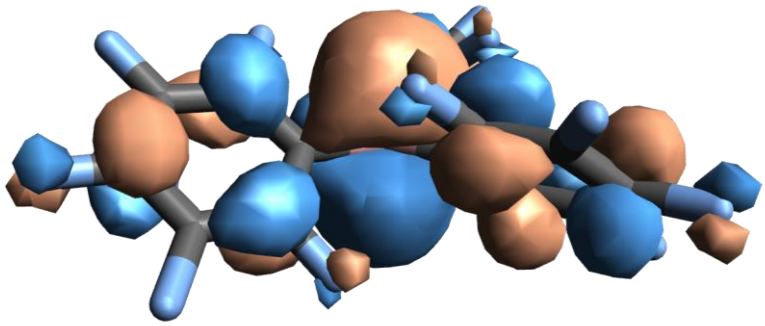


Figure S53. Side view representation of LUMO of $B(C_6F_5)_3$ at B3LYP/def2-TZVP level of theory.

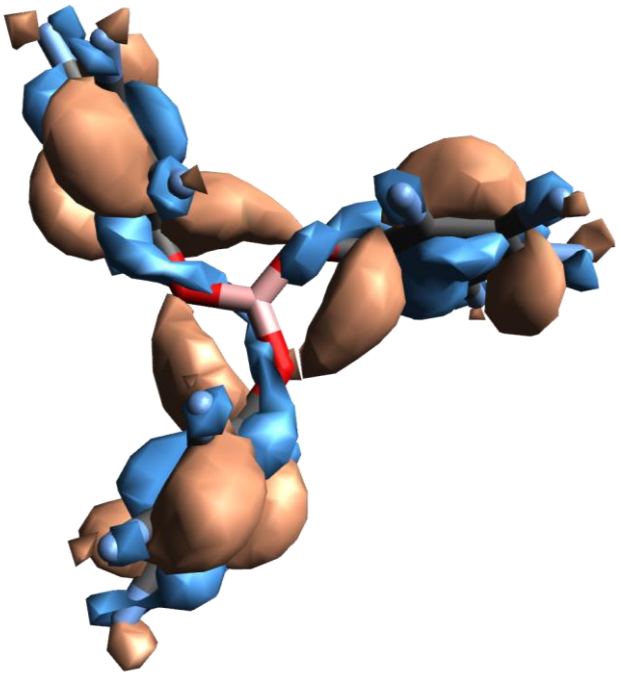


Figure S54. Top view representation of LUMO of $B(OC_6F_5)_3$ at B3LYP/def2-TZVP level of theory.

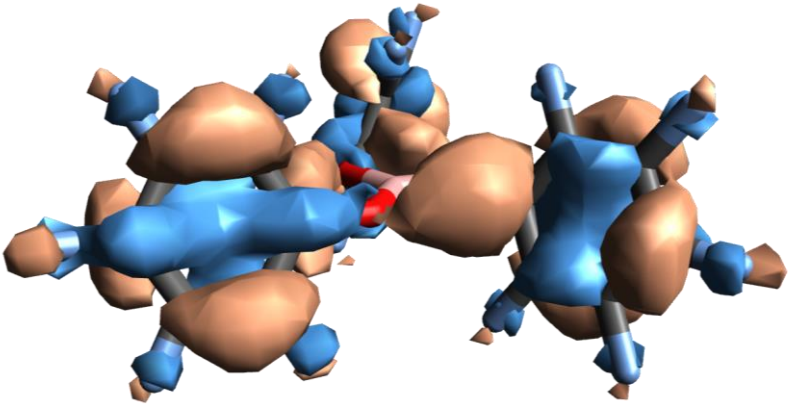


Figure S55. Side view representation of LUMO of $B(OC_6F_5)_3$ at B3LYP/def2-TZVP level of theory.

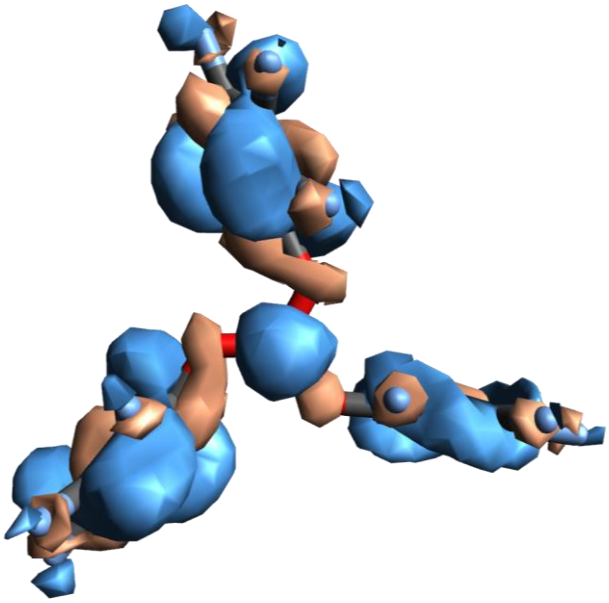


Figure S56. Top view representation of LUMO+1 of $B(OC_6F_5)_3$ at B3LYP/def2-TZVP level of theory.

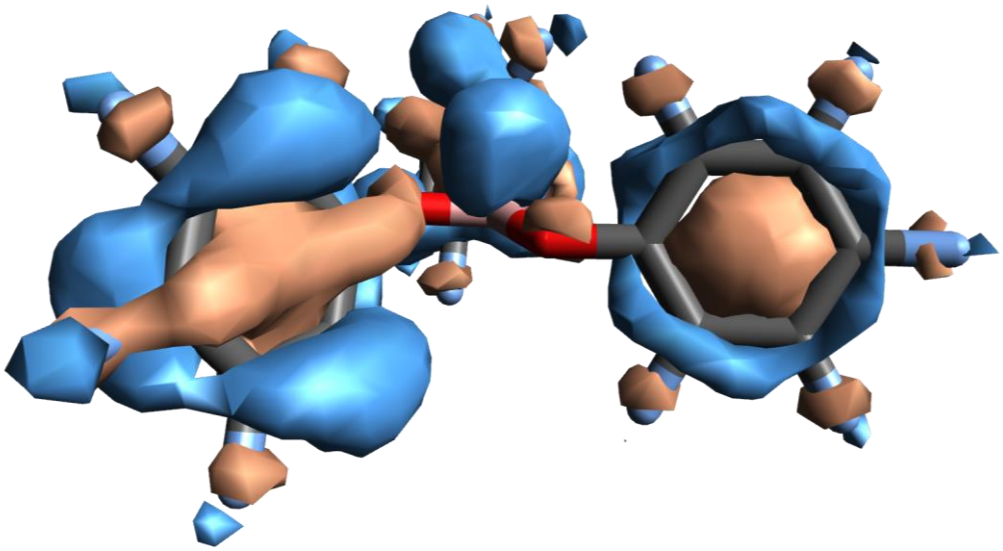


Figure S57. Side view representation of LUMO+1 of $B(OC_6F_5)_3$ at B3LYP/def2-TZVP level of theory.

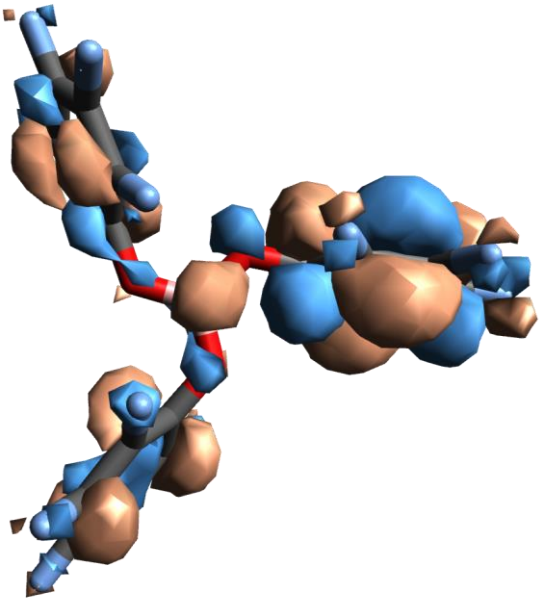


Figure S58. Top view representation of LUMO+2 of $B(OC_6F_5)_3$ at B3LYP/def2-TZVP level of theory.

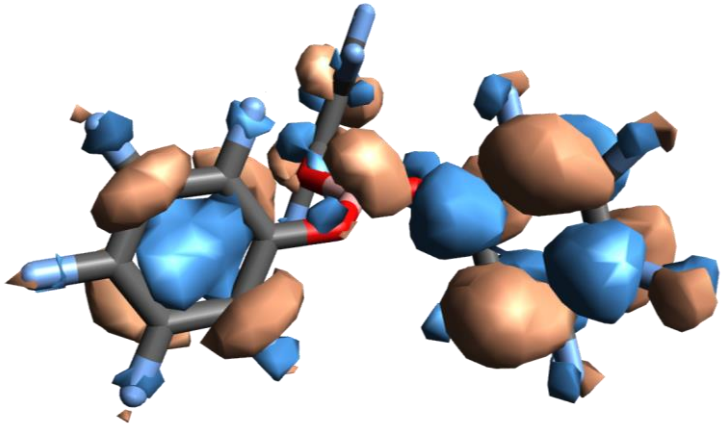


Figure S59. Side view representation of LUMO+2 of $B(OC_6F_5)_3$ at B3LYP/def2-TZVP level of theory.

6.5 Graphical representation of Lewis acidity trends

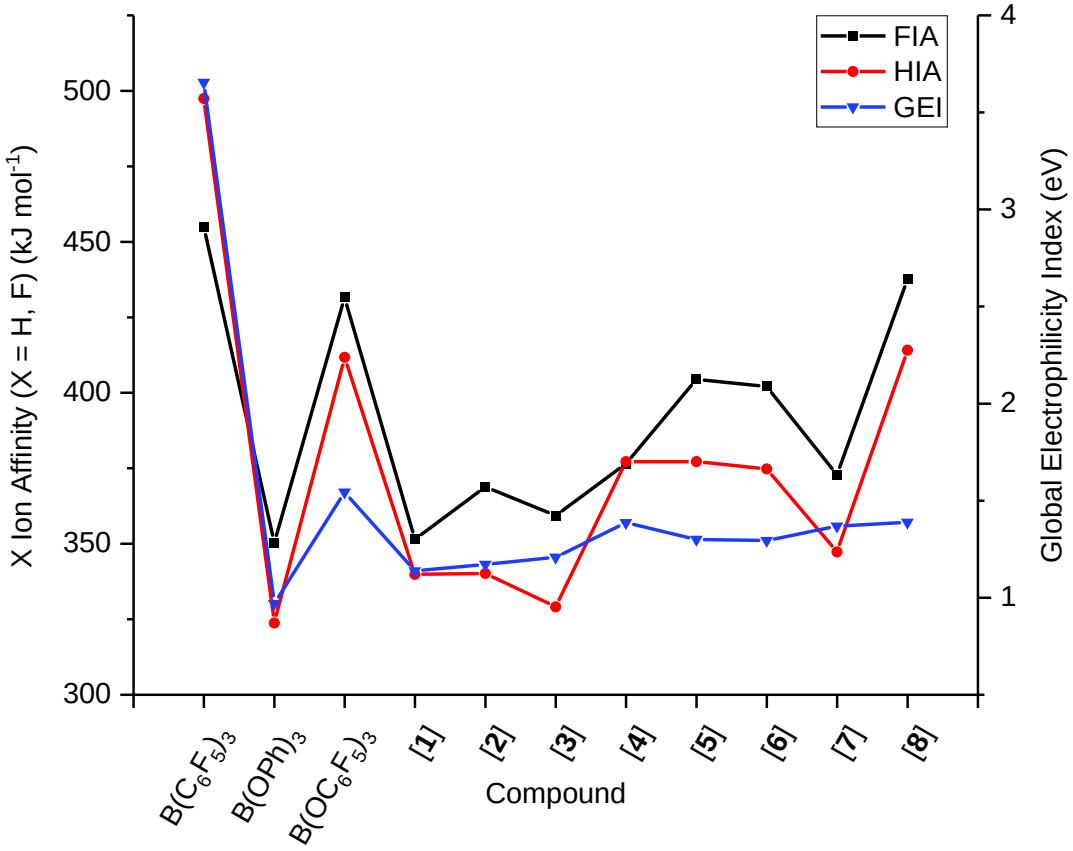


Figure S60. Comparison of GEI, HIA and FIA values for boranes and borates.

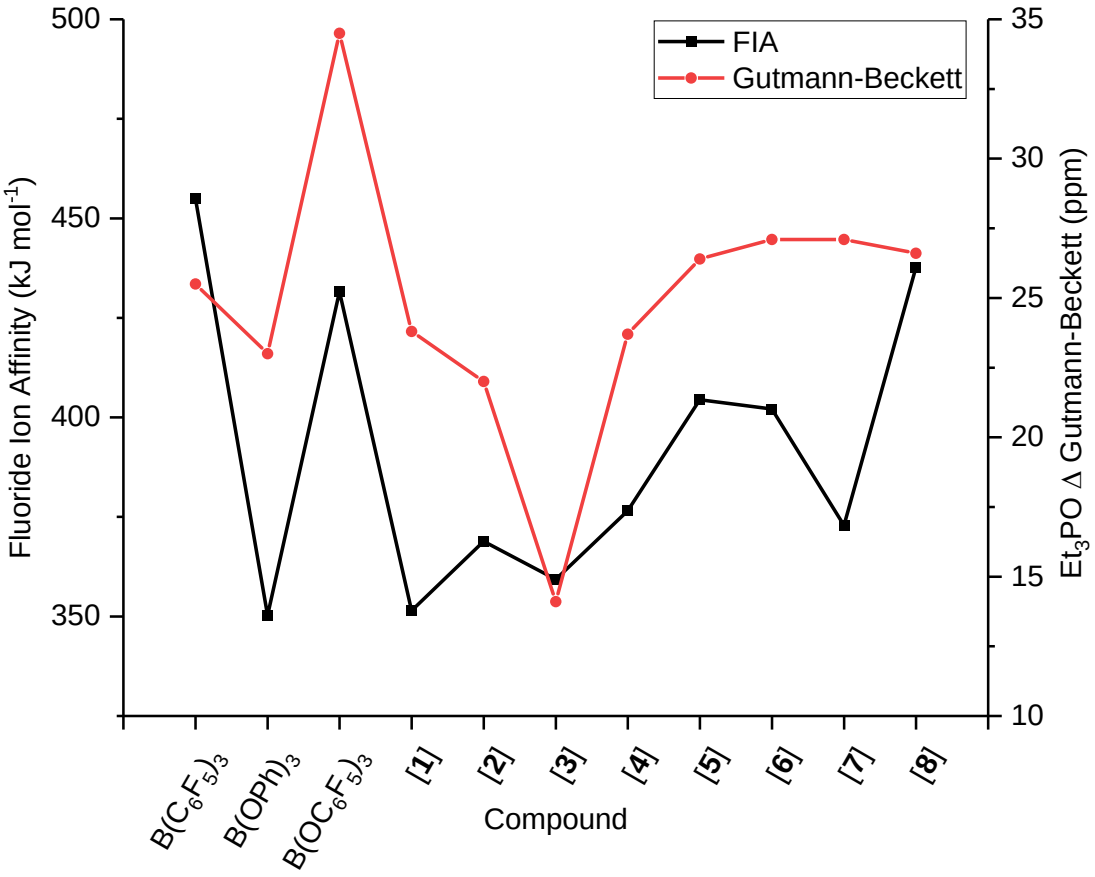


Figure S61. Comparison of FIA and Gutmann-Beckett Lewis acidity metrics for boranes and borates.

6.6 Cartesian coordinates for optimised structures

Table S6. Cartesian coordinates of optimised $B(C_6F_5)_3$ at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	-0.0370490000	-0.1217400000	-0.1159340000
C	0.3873370000	1.3703320000	-0.2544550000
C	0.0159680000	2.1359990000	-1.3516630000
C	0.3712670000	3.4640360000	-1.4817020000
C	1.1075440000	4.0645800000	-0.4736740000
C	1.4905690000	3.3378060000	0.6411560000
C	1.1373160000	2.0053790000	0.7263510000
F	1.5021040000	1.3334620000	1.8135560000
F	2.1826590000	3.9246820000	1.6059510000
F	1.4457530000	5.3363540000	-0.5759580000
F	0.0179580000	4.1659030000	-2.5478220000
F	-0.6776320000	1.5763940000	-2.3377210000
C	-1.4916300000	-0.5491120000	-0.4702000000
C	-1.7604400000	-1.7306990000	-1.1496540000
C	-3.0441360000	-2.1260820000	-1.4698450000
C	-4.1088920000	-1.3285470000	-1.0839400000
C	-3.8851480000	-0.1473350000	-0.3967170000
C	-2.5867400000	0.2277920000	-0.1126560000
F	-2.4029000000	1.3575480000	0.5625460000
F	-4.9108780000	0.6022490000	-0.0223740000
F	-5.3432430000	-1.6952690000	-1.3727540000
F	-3.2679020000	-3.2492060000	-2.1351650000
F	-0.7554780000	-2.5049970000	-1.5449360000
C	0.9869490000	-1.1762200000	0.3972930000
C	2.3118270000	-1.1706340000	-0.0208900000
C	3.2352030000	-2.0927360000	0.4309410000
C	2.8363050000	-3.0475810000	1.3514780000

C	1.5265480000	-3.0831200000	1.8000510000
C	0.6249860000	-2.1589770000	1.3100970000
F	-0.6205060000	-2.2034540000	1.7715440000
F	1.1574840000	-3.9942110000	2.6876640000
F	3.7089400000	-3.9278840000	1.8042530000
F	4.4876110000	-2.0746680000	0.0003200000
F	2.7161640000	-0.2744920000	-0.9147820000

Table S7. Cartesian coordinates of optimised $B(OPh)_3$ at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	-0.0088610000	-0.0073070000	0.0352430000
O	-1.2508250000	0.5367610000	0.1010510000
C	-2.4093940000	-0.1720320000	0.2238580000
C	-2.8196690000	-1.0542700000	-0.7653400000
C	-4.0277090000	-1.7196810000	-0.6276070000
C	-4.8275170000	-1.5071090000	0.4853040000
C	-4.4113750000	-0.6171140000	1.4639400000
C	-3.2040540000	0.0522980000	1.3377930000
O	1.0772600000	0.7915800000	-0.1233460000
C	1.0400920000	2.1462640000	-0.2741180000
C	0.3775610000	2.7358170000	-1.3412900000
C	0.4026380000	4.1144820000	-1.4814910000
C	1.0863830000	4.9050360000	-0.5698790000
C	1.7528760000	4.3046800000	0.4875650000
C	1.7324340000	2.9269490000	0.6392830000
O	0.1501700000	-1.3518720000	0.1340760000
C	1.3571680000	-1.9874960000	0.1099430000
C	1.6552520000	-2.8102450000	-0.9651920000
C	2.8565350000	-3.5019330000	-0.9857510000
C	3.7582710000	-3.3751970000	0.0599210000
C	3.4472950000	-2.5537180000	1.1334050000

C	2.2483260000	-1.8593380000	1.1650260000
H	4.1419820000	-2.4514310000	1.9565910000
H	4.6947650000	-3.9158130000	0.0409630000
H	3.0870480000	-4.1429140000	-1.8263990000
H	0.9459670000	-2.9098520000	-1.7765100000
H	2.0042920000	-1.2260540000	2.0080730000
H	-2.8764370000	0.7520480000	2.0954380000
H	-0.1518960000	2.1255210000	-2.0609460000
H	-0.1168980000	4.5718360000	-2.3130820000
H	1.1030830000	5.9801850000	-0.6857420000
H	2.2937740000	4.9104960000	1.2024980000
H	2.2557400000	2.4525080000	1.4591740000
H	-5.0288170000	-0.4402850000	2.3346640000
H	-4.3445920000	-2.4089490000	-1.3991120000
H	-5.7696650000	-2.0283760000	0.5867130000
H	-2.2036220000	-1.2195930000	-1.6395850000

Table S8. Cartesian coordinates of optimised $B(OC_6F_5)_3$ at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	0.0077020000	0.0394810000	0.0642480000
O	-1.2097360000	0.6311290000	0.1700070000
C	-2.3427730000	-0.0993000000	0.2846750000
C	-2.9439730000	-0.6482300000	-0.8362190000
C	-4.1274300000	-1.3547770000	-0.7273990000
C	-4.7177620000	-1.5167260000	0.5142790000
C	-4.1207930000	-0.9795160000	1.6416840000
C	-2.9352600000	-0.2763550000	1.5236260000
F	-2.3528250000	0.2259690000	2.6016540000
F	-4.6821770000	-1.1443490000	2.8290970000
F	-5.8516410000	-2.1897710000	0.6240740000
F	-4.6940670000	-1.8772910000	-1.8034380000

F	-2.3666200000	-0.5001120000	-2.0191800000
O	1.1223550000	0.7931500000	-0.1183140000
C	1.0650440000	2.1289510000	-0.3190200000
C	0.5722540000	2.6464770000	-1.5061180000
C	0.5575890000	4.0099760000	-1.7317600000
C	1.0500040000	4.8692960000	-0.7644550000
C	1.5482250000	4.3633580000	0.4234780000
C	1.5502710000	2.9972090000	0.6449070000
F	2.0150620000	2.5136190000	1.7857440000
F	2.0174750000	5.1885550000	1.3460100000
F	1.0423590000	6.1755660000	-0.9748750000
F	0.0785270000	4.4940480000	-2.8666320000
F	0.1045580000	1.8151800000	-2.4268300000
O	0.1051060000	-1.3114870000	0.1533640000
C	1.2893610000	-1.9619440000	0.1435200000
C	1.6738870000	-2.6875480000	-0.9714570000
C	2.8486420000	-3.4182220000	-0.9619880000
C	3.6507660000	-3.4184520000	0.1659290000
C	3.2814330000	-2.6855960000	1.2810000000
C	2.1032600000	-1.9628790000	1.2644220000
F	1.7398900000	-1.2564510000	2.3254360000
F	4.0525170000	-2.6818700000	2.3565750000
F	4.7729190000	-4.1190270000	0.1774740000
F	3.2080960000	-4.1156800000	-2.0280080000
F	0.9086610000	-2.6776460000	-2.0514500000

Table S9. Cartesian coordinates of optimised B(O(2-FC_6H_4))$_3$ [**1**] at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	-0.6323600000	-0.6448150000	0.5897340000
O	0.3758880000	-1.0984990000	1.3877340000
C	1.6718600000	-1.1518470000	0.9913160000

C	2.0284770000	-1.9365710000	-0.0966960000
C	3.3354200000	-2.0358850000	-0.5217420000
C	4.3183570000	-1.3374560000	0.1639560000
C	3.9811460000	-0.5582510000	1.2606680000
C	2.6618320000	-0.4658930000	1.6753290000
H	2.3865480000	0.1459020000	2.5236410000
H	4.7466150000	-0.0128610000	1.7949480000
H	5.3472030000	-1.4058450000	-0.1612940000
H	3.5724990000	-2.6505110000	-1.3795970000
F	1.0572440000	-2.5898830000	-0.7452380000
O	-1.8519060000	-1.1988700000	0.8123160000
C	-2.9994360000	-0.6759800000	0.3154690000
C	-3.7984940000	-1.4167580000	-0.5383860000
C	-4.9993440000	-0.8952390000	-0.9971490000
C	-5.4066030000	0.3704070000	-0.6062950000
C	-4.6137480000	1.1207580000	0.2506470000
C	-3.4262110000	0.5872320000	0.7008850000
F	-2.6508390000	1.2941410000	1.5356940000
H	-4.9107860000	2.1098670000	0.5724140000
H	-6.3414940000	0.7789230000	-0.9639310000
H	-5.6153350000	-1.4825330000	-1.6639830000
H	-3.4711090000	-2.4043460000	-0.8351940000
O	-0.4953510000	0.3097750000	-0.3730150000
C	0.5453640000	1.1823770000	-0.4149070000
C	1.4790450000	1.0870670000	-1.4376820000
C	2.5560180000	1.9450780000	-1.5072090000
C	2.7001410000	2.9331050000	-0.5443700000
C	1.7633590000	3.0551450000	0.4694380000
C	0.6859060000	2.1845290000	0.5317790000
H	-0.0559320000	2.2794910000	1.3140460000

H	1.8658690000	3.8311800000	1.2154580000
H	3.5433630000	3.6080400000	-0.5937760000
H	3.2735620000	1.8317020000	-2.3085290000
F	1.3344550000	0.1278730000	-2.3522910000

Table S10. Cartesian coordinates of optimised $B(O(3\text{-}FC_6H_4))_3$ [**2**] at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	-0.0256280000	0.0205410000	-0.1287710000
O	-0.2473630000	1.3599900000	-0.1421770000
C	0.7191170000	2.3160220000	-0.0716490000
C	1.5548310000	2.3973240000	1.0328670000
C	2.4844150000	3.4175000000	1.0759790000
C	2.6075570000	4.3524590000	0.0669980000
C	1.7555650000	4.2509910000	-1.0219980000
C	0.8106830000	3.2403340000	-1.1016460000
H	0.1438770000	3.1680100000	-1.9498460000
H	1.8304440000	4.9729640000	-1.8236790000
H	3.3468090000	5.1381300000	0.1358820000
F	3.2890740000	3.4977410000	2.1397760000
H	1.4893120000	1.6899800000	1.8486910000
O	1.2472600000	-0.4505910000	-0.1292840000
C	1.6219170000	-1.7568270000	-0.0568300000
C	2.5111280000	-2.2187570000	-1.0159480000
C	2.9469550000	-3.5263580000	-0.9330280000
C	2.5277320000	-4.3842530000	0.0646350000
C	1.6428570000	-3.8954150000	1.0129490000
C	1.1862490000	-2.5878450000	0.9664110000
H	0.5028060000	-2.2250280000	1.7213420000
H	1.3034420000	-4.5464610000	1.8069450000
H	2.8882700000	-5.4027270000	0.0992390000
F	3.8055160000	-3.9718060000	-1.8546860000

H	2.8608460000	-1.5673550000	-1.8056150000
O	-1.0725390000	-0.8433190000	-0.1345000000
C	-2.3889290000	-0.5134400000	-0.0406120000
C	-2.8737900000	0.2696860000	0.9983580000
C	-4.2335780000	0.5263870000	1.0709240000
C	-5.1151170000	0.0122630000	0.1328620000
C	-4.5983190000	-0.7691960000	-0.8817320000
C	-3.2493350000	-1.0435290000	-0.9906940000
H	-2.8730190000	-1.6638770000	-1.7930500000
F	-5.4288640000	-1.2820430000	-1.7940070000
H	-6.1768440000	0.2076180000	0.1878640000
H	-4.6143140000	1.1380100000	1.8774490000
H	-2.2051500000	0.6740380000	1.7455170000

Table S11. Cartesian coordinates of optimised $B(O(4\text{-}FC_6H_4))_3$ [**3**] at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	0.0334490000	-0.0293050000	0.0244580000
O	-0.2123900000	1.3047010000	0.0120860000
C	0.7200060000	2.2991500000	0.0094810000
C	1.6786830000	2.4085960000	1.0066350000
C	2.5676720000	3.4721790000	0.9973120000
C	2.4820130000	4.4147030000	-0.0081890000
C	1.5323330000	4.3204460000	-1.0060220000
C	0.6476440000	3.2543800000	-0.9934620000
H	-0.1100150000	3.1667910000	-1.7606830000
H	1.4818040000	5.0715110000	-1.7824780000
F	3.3343650000	5.4462400000	-0.0131380000
H	3.3187450000	3.5679790000	1.7695610000
H	1.7375050000	1.6730180000	1.7972800000
O	1.3094770000	-0.4928370000	0.0366900000
C	1.6540320000	-1.8137780000	0.0436310000

C	2.4209590000	-2.3007860000	-1.0036550000
C	2.8267540000	-3.6260100000	-1.0116000000
C	2.4560380000	-4.4466690000	0.0350310000
C	1.6985930000	-3.9750590000	1.0889640000
C	1.2977530000	-2.6486650000	1.0927840000
H	0.7082540000	-2.2723400000	1.9179590000
H	1.4239970000	-4.6362230000	1.8995450000
F	2.8419370000	-5.7277590000	0.0304200000
H	3.4244560000	-4.0161670000	-1.8240840000
H	2.7049320000	-1.6400870000	-1.8118820000
O	-1.0059930000	-0.9032430000	0.0209540000
C	-2.3210950000	-0.5394200000	0.0055320000
C	-2.8868430000	0.1644260000	1.0585550000
C	-4.2347460000	0.4841380000	1.0326930000
C	-4.9995270000	0.0896880000	-0.0473970000
C	-4.4531910000	-0.6193340000	-1.0986840000
C	-3.1038280000	-0.9342920000	-1.0683730000
H	-2.6571380000	-1.4934550000	-1.8797090000
H	-5.0727670000	-0.9218620000	-1.9318660000
F	-6.3008900000	0.3994610000	-0.0734180000
H	-4.6864090000	1.0352240000	1.8462390000
H	-2.2826980000	0.4658250000	1.9037660000

Table S12. Cartesian coordinates of optimised $B(O(2,4\text{-}F_2C_6H_3))_3$ [**4**] at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	0.7372270000	0.6596790000	-0.6906480000
O	-0.2404920000	1.1613200000	-1.4944340000
C	-1.5410920000	1.2709540000	-1.1216560000
C	-1.9585690000	2.2542290000	-0.2399010000
C	-3.2879810000	2.3530570000	0.1423530000
C	-4.1955960000	1.4545340000	-0.3801990000

C	-3.8189980000	0.4753410000	-1.2801100000
C	-2.4916620000	0.4052240000	-1.6470220000
F	-2.1011980000	-0.5340090000	-2.5038640000
H	-4.5395730000	-0.2209940000	-1.6868650000
F	-5.4771880000	1.5285790000	-0.0146090000
H	-3.6117280000	3.1191760000	0.8327400000
O	0.5427850000	-0.1238090000	0.4081600000
C	-0.5726050000	-0.8579510000	0.6623170000
C	-1.4272660000	-0.5237960000	1.6997530000
C	-2.5525510000	-1.2864820000	1.9657280000
C	-2.8047910000	-2.3951740000	1.1813730000
C	-1.9671620000	-2.7653430000	0.1473910000
C	-0.8541250000	-1.9867910000	-0.0943790000
F	-0.0358400000	-2.3072770000	-1.0938740000
H	-2.1727250000	-3.6352830000	-0.4612670000
F	-3.8891770000	-3.1347920000	1.4239570000
H	-3.2253600000	-1.0201940000	2.7684720000
O	1.9955920000	1.0667220000	-0.9973930000
C	3.1065740000	0.5822780000	-0.3860780000
C	3.8595490000	1.3857230000	0.4522550000
C	5.0288440000	0.9145790000	1.0311730000
C	5.4314800000	-0.3764800000	0.7564680000
C	4.7050080000	-1.2067700000	-0.0762250000
C	3.5489060000	-0.7087390000	-0.6393900000
F	2.8316520000	-1.4815700000	-1.4522560000
H	5.0303270000	-2.2161890000	-0.2878870000
F	6.5559710000	-0.8446130000	1.3040270000
H	5.6171920000	1.5439830000	1.6837860000
H	-1.2104990000	0.3503680000	2.2981890000
H	-1.2311450000	2.9532670000	0.1524940000

H	3.5286460000	2.3973930000	0.6452360000

Table S13. Cartesian coordinates of optimised $B(O(3,5\text{-}F_2C_6H_3))_3$ [**5**] at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	0.0144000000	0.0134300000	0.1450100000
O	-0.2318490000	1.3478670000	0.1573430000
C	0.7233950000	2.3148640000	0.1066920000
C	1.6273170000	2.4770250000	1.1461350000
C	2.5463510000	3.5035490000	1.0470660000
C	2.5970380000	4.3662640000	-0.0304080000
C	1.6715010000	4.1655120000	-1.0357130000
C	0.7303690000	3.1559920000	-0.9954830000
H	0.0146930000	3.0305290000	-1.7960780000
F	1.6900410000	4.9777160000	-2.0919830000
H	3.3255620000	5.1630300000	-0.0818960000
F	3.4251730000	3.6697450000	2.0350890000
H	1.6221800000	1.8301140000	2.0122170000
O	1.2926160000	-0.4429810000	0.1538350000
C	1.6320460000	-1.7593600000	0.0937070000
C	2.1998520000	-2.2372480000	-1.0770460000
C	2.5815300000	-3.5639500000	-1.1171920000
C	2.4207510000	-4.4219830000	-0.0468100000
C	1.8531600000	-3.8957830000	1.0973700000
C	1.4514400000	-2.5780910000	1.1979690000
H	1.0169000000	-2.2055120000	2.1152190000
F	1.6864400000	-4.6953860000	2.1504800000
H	2.7283710000	-5.4567520000	-0.1002640000
F	3.1257350000	-4.0375660000	-2.2376730000
H	2.3490930000	-1.5895590000	-1.9298280000
O	-1.0157770000	-0.8693800000	0.1139220000
C	-2.3315400000	-0.5350260000	0.0381550000

C	-2.9520200000	0.1440110000	1.0761530000
C	-4.3015470000	0.4126590000	0.9557800000
C	-5.0482070000	0.0348350000	-0.1430340000
C	-4.3844960000	-0.6437070000	-1.1463750000
C	-3.0371320000	-0.9399390000	-1.0849870000
H	-2.5491060000	-1.4800640000	-1.8844290000
F	-5.0745140000	-1.0267150000	-2.2202330000
H	-6.1039320000	0.2558920000	-0.2122030000
F	-4.9117960000	1.0641320000	1.9453910000
H	-2.4101680000	0.4530010000	1.9590430000

Table S14. Cartesian coordinates of optimised $B(O(2,3,4\text{-}F_3C_6H_2))_3$ [**6**] at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	0.0307370000	-0.0334490000	0.0521670000
O	-0.2872950000	1.2853640000	0.0858260000
C	0.6237560000	2.2870610000	0.1598350000
C	0.6976860000	3.0935110000	1.2809250000
C	1.5818020000	4.1612230000	1.3179580000
C	2.3895190000	4.4180730000	0.2305720000
C	2.3274990000	3.6163380000	-0.8976130000
C	1.4421010000	2.5551000000	-0.9277610000
F	1.3732620000	1.7882460000	-2.0097240000
F	3.1021250000	3.8625240000	-1.9449870000
F	3.2399700000	5.4409020000	0.2430880000
H	1.6432180000	4.7983340000	2.1889000000
H	0.0509810000	2.8887100000	2.1227740000
O	1.3193970000	-0.4364490000	0.2029370000
C	1.6903330000	-1.7374950000	0.0871950000
C	1.5923670000	-2.3772200000	-1.1401680000
C	1.9980990000	-3.6903290000	-1.2856020000
C	2.5154310000	-4.3670710000	-0.1931440000

C	2.6247920000	-3.7407250000	1.0300980000
C	2.2102220000	-2.4245160000	1.1688310000
H	2.2923200000	-1.9239300000	2.1234090000
H	3.0307740000	-4.2839040000	1.8717470000
F	2.9022740000	-5.6304940000	-0.3472930000
F	1.8895560000	-4.2894310000	-2.4635390000
F	1.0945770000	-1.7271770000	-2.1868600000
O	-0.9560410000	-0.9565320000	-0.0976370000
C	-2.2694890000	-0.6163540000	-0.1045690000
C	-2.8584120000	-0.1411310000	1.0581590000
C	-4.2017080000	0.1800130000	1.0890180000
C	-4.9650080000	0.0131390000	-0.0552150000
C	-4.3939300000	-0.4671570000	-1.2144980000
C	-3.0431290000	-0.7810900000	-1.2384860000
H	-2.5839950000	-1.1577870000	-2.1418040000
H	-5.0056850000	-0.5913670000	-2.0968950000
F	-6.2570090000	0.3265970000	-0.0130470000
F	-4.7466890000	0.6428580000	2.2060930000
F	-2.1205350000	0.0167820000	2.1542500000

Table S15. Cartesian coordinates of optimised $B(O(2,4,6\text{-}F_3C_6H_2))_3$ [**7**] at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	0.7151220000	0.5252490000	-0.8567390000
O	-0.3047550000	0.9185660000	-1.6697140000
C	-1.5596330000	1.1339440000	-1.2158390000
C	-1.8386380000	2.1685630000	-0.3344670000
C	-3.1111650000	2.4228900000	0.1347200000
C	-4.1315920000	1.6083240000	-0.3150200000
C	-3.9164340000	0.5694480000	-1.2003380000
C	-2.6260140000	0.3534630000	-1.6397110000
F	-2.3786030000	-0.6478420000	-2.4759850000

H	-4.7280410000	-0.0585980000	-1.5399640000
F	-5.3698730000	1.8302780000	0.1233440000
H	-3.2952990000	3.2322320000	0.8271880000
F	-0.8202170000	2.9180580000	0.0786940000
O	0.5642290000	-0.1356900000	0.3291850000
C	-0.5285950000	-0.8634490000	0.6512790000
C	-1.3428080000	-0.5059240000	1.7162190000
C	-2.4495670000	-1.2475750000	2.0755810000
C	-2.7308370000	-2.3839360000	1.3414290000
C	-1.9512850000	-2.7923830000	0.2771540000
C	-0.8544480000	-2.0191520000	-0.0428780000
F	-0.0775070000	-2.3643420000	-1.0663240000
H	-2.1853230000	-3.6838020000	-0.2876650000
F	-3.7956700000	-3.1120510000	1.6725240000
H	-3.0729020000	-0.9439810000	2.9048970000
F	-1.0464940000	0.5990650000	2.3894020000
O	1.9641570000	0.8276210000	-1.2875380000
C	3.0585630000	0.4633070000	-0.5787500000
C	3.4846340000	1.1972840000	0.5175080000
C	4.6176830000	0.8684610000	1.2333380000
C	5.3348830000	-0.2383930000	0.8230290000
C	4.9568790000	-1.0084060000	-0.2592390000
C	3.8144810000	-0.6396150000	-0.9425290000
F	3.4088910000	-1.3641940000	-1.9791840000
H	5.5288950000	-1.8735740000	-0.5637490000
F	6.4299250000	-0.5787390000	1.5016960000
H	4.9259910000	1.4579470000	2.0853010000
F	2.7570250000	2.2470040000	0.8848760000

Table S16. Cartesian coordinates of optimised $B(O(3,4,5\text{-}F_3C_6H_2))_3$ [**8**] at M06-2X/def2-QZVPP (used in FIA/HIA calculations)

B	0.0270630000	-0.0243430000	-0.0033490000
O	-0.1970540000	1.3131450000	-0.0219930000
C	0.7340680000	2.3028010000	-0.0135940000
C	1.6977780000	2.3853740000	0.9804480000
C	2.5716410000	3.4545550000	0.9659800000
C	2.5044720000	4.4353800000	-0.0075770000
C	1.5318580000	4.3259480000	-0.9856510000
C	0.6441130000	3.2698690000	-1.0030010000
H	-0.1147380000	3.2115020000	-1.7710110000
F	1.4605610000	5.2645350000	-1.9219770000
F	3.3477290000	5.4600980000	-0.0001900000
F	3.5010300000	3.5572530000	1.9089610000
H	1.7785410000	1.6469400000	1.7657670000
O	1.2956080000	-0.5070500000	0.0185130000
C	1.6488670000	-1.8211770000	0.0263740000
C	2.5616380000	-2.2435960000	-0.9278460000
C	2.9720210000	-3.5614020000	-0.9203000000
C	2.4897660000	-4.4628590000	0.0119760000
C	1.5843130000	-4.0116030000	0.9554830000
C	1.1576920000	-2.6990280000	0.9815540000
H	0.4559540000	-2.3884160000	1.7425430000
F	1.1208200000	-4.8717780000	1.8548490000
F	2.8882580000	-5.7286150000	0.0043050000
F	3.8457180000	-3.9870220000	-1.8248940000
H	2.9557320000	-1.5570110000	-1.6643850000
O	-1.0268330000	-0.8804340000	-0.0137200000
C	-2.3391050000	-0.5240930000	0.0023380000
C	-2.8574060000	0.2619340000	1.0207040000

C	-4.2066490000	0.5524520000	1.0110740000
C	-5.0444900000	0.0751830000	0.0189130000
C	-4.5007190000	-0.7153250000	-0.9780000000
C	-3.1548360000	-1.0208640000	-1.0021290000
H	-2.7536990000	-1.6453080000	-1.7885190000
F	-5.3021650000	-1.1830880000	-1.9275550000
F	-6.3393940000	0.3650860000	0.0263570000
F	-4.7247980000	1.3049810000	1.9747820000
H	-2.2394830000	0.6471380000	1.8197070000

Table S17. Cartesian coordinates of optimised F-ion adduct F–B(C_6F_5)$_3$ at M06-2X/def2-QZVPP (used in FIA calculations)

B	-0.0097220000	0.0239650000	0.8305520000
C	-1.4900310000	0.5440640000	0.3228850000
C	-2.0761560000	1.6364830000	0.9461790000
C	-3.3355300000	2.1116800000	0.6260940000
C	-4.0632100000	1.4888040000	-0.3696270000
C	-3.5132670000	0.4117500000	-1.0323550000
C	-2.2490940000	-0.0327060000	-0.6792600000
F	-1.7827440000	-1.0639310000	-1.3926650000
F	-4.2023880000	-0.1883410000	-2.0056740000
F	-5.2792470000	1.9305220000	-0.6923290000
F	-3.8553410000	3.1670050000	1.2573330000
F	-1.4135570000	2.3143490000	1.8842990000
C	0.2741830000	-1.5261520000	0.3423050000
C	1.1421120000	-1.9101730000	-0.6640200000
C	1.3741290000	-3.2315170000	-1.0094130000
C	0.7140070000	-4.2353130000	-0.3315030000
C	-0.1779170000	-3.9011840000	0.6687450000
C	-0.3842910000	-2.5682290000	0.9781950000
F	-1.2974320000	-2.3185720000	1.9178570000

F	-0.8342320000	-4.8679890000	1.3143770000
F	0.9259910000	-5.5136860000	-0.6456870000
F	2.2231060000	-3.5454560000	-1.9908670000
F	1.7996970000	-0.9993990000	-1.3907650000
C	1.1987000000	1.0308710000	0.3365530000
C	1.0969030000	2.0192580000	-0.6249150000
C	2.1479880000	2.8512980000	-0.9775630000
C	3.3701690000	2.7013200000	-0.3564020000
C	3.5242700000	1.7195670000	0.6032380000
C	2.4488400000	0.9122670000	0.9264380000
F	2.6802500000	-0.0429410000	1.8284790000
F	4.7101070000	1.5591230000	1.1947680000
F	4.3960430000	3.4871400000	-0.6846860000
F	1.9938650000	3.7918710000	-1.9123150000
F	-0.0428380000	2.2120030000	-1.2982590000
F	-0.0137620000	0.0329360000	2.2399470000

Table S18. Cartesian coordinates of optimised F-ion adduct F–B(OPh)$_3$ at M06-2X/def2-QZVPP (used in FIA calculations)

B	-0.2331040000	0.2188710000	1.2780400000
O	-1.5583190000	0.6795430000	0.8729920000
C	-2.5979820000	-0.0854230000	0.5838870000
C	-3.6626280000	0.5126180000	-0.1043810000
C	-4.7984340000	-0.2064680000	-0.4318920000
C	-4.9131310000	-1.5465520000	-0.0876050000
C	-3.8636850000	-2.1447990000	0.5960890000
C	-2.7212140000	-1.4373790000	0.9343180000
O	0.6434330000	1.3858600000	1.3357560000
C	0.9305540000	2.2069240000	0.3387930000
C	0.5130820000	2.0453820000	-0.9901140000
C	0.8822790000	2.9696190000	-1.9547710000

C	1.6653560000	4.0724180000	-1.6454760000
C	2.0824520000	4.2366690000	-0.3314780000
C	1.7227470000	3.3232880000	0.6428730000
O	0.1934730000	-0.7743920000	0.2816770000
C	1.3257000000	-1.4580410000	0.2797350000
C	1.4709600000	-2.4476960000	-0.7028670000
C	2.6235480000	-3.2069450000	-0.7903270000
C	3.6717750000	-3.0093960000	0.0988120000
C	3.5344570000	-2.0322510000	1.0741430000
C	2.3856080000	-1.2632070000	1.1758160000
H	4.3402200000	-1.8582190000	1.7776650000
H	4.5752580000	-3.6017180000	0.0314060000
H	2.7023940000	-3.9627420000	-1.5631310000
H	0.6540800000	-2.6046550000	-1.3962860000
H	2.3190970000	-0.5070570000	1.9439320000
H	-1.9294070000	-1.9340630000	1.4752720000
H	-0.0910960000	1.1976040000	-1.2755000000
H	0.5466880000	2.8173970000	-2.9739290000
H	1.9456540000	4.7853630000	-2.4102430000
H	2.6961130000	5.0875320000	-0.0590020000
H	2.0496330000	3.4562970000	1.6666840000
H	-3.9314940000	-3.1890900000	0.8779170000
H	-5.6019210000	0.2871660000	-0.9662140000
H	-5.7997910000	-2.1115220000	-0.3452810000
H	-3.5729870000	1.5563270000	-0.3791570000
F	-0.2364030000	-0.3327470000	2.5579390000

Table S19. Cartesian coordinates of optimised F-ion adduct F–B(OC_6F_5)$_3$ at M06-2X/def2-QZVPP (used in FIA calculations)

B	0.1272410000	0.4620510000	1.3184300000
O	-0.6295720000	0.7006600000	0.0643430000

C	-1.8832740000	1.0987390000	0.0511900000
C	-2.8692680000	0.2862030000	-0.5110250000
C	-4.1927850000	0.6778550000	-0.5831000000
C	-4.5779560000	1.9055680000	-0.0803300000
C	-3.6247510000	2.7335860000	0.4820100000
C	-2.3015760000	2.3372040000	0.5423470000
F	-1.4157450000	3.1716100000	1.0695210000
F	-3.9889840000	3.9229820000	0.9602050000
F	-5.8541740000	2.2895330000	-0.1404230000
F	-5.1029450000	-0.1293560000	-1.1270170000
F	-2.5334440000	-0.9072580000	-0.9971050000
O	0.7636410000	-0.8600700000	1.1898440000
C	0.2566950000	-1.7956520000	0.4091210000
C	-0.6445360000	-2.7440340000	0.8873630000
C	-1.1550890000	-3.7372830000	0.0711510000
C	-0.7787310000	-3.8060650000	-1.2557710000
C	0.1178200000	-2.8801870000	-1.7560170000
C	0.6227660000	-1.8935610000	-0.9328130000
F	1.4859900000	-1.0189750000	-1.4386170000
F	0.4880000000	-2.9458170000	-3.0345010000
F	-1.2696790000	-4.7603050000	-2.0475940000
F	-2.0156740000	-4.6300560000	0.5600710000
F	-1.0315130000	-2.7027110000	2.1572900000
O	1.1885440000	1.4479180000	1.4993770000
C	2.3339850000	1.3320520000	0.8544730000
C	3.4092590000	0.6438960000	1.4180310000
C	4.6294730000	0.5470760000	0.7773720000
C	4.8110720000	1.1364760000	-0.4595560000
C	3.7652250000	1.8267840000	-1.0404750000
C	2.5465340000	1.9197700000	-0.3920330000

F	1.5691190000	2.6007120000	-0.9774930000
F	3.9379010000	2.4033860000	-2.2299570000
F	5.9883810000	1.0466780000	-1.0807610000
F	5.6382620000	-0.1127920000	1.3476580000
F	3.2717140000	0.0788840000	2.6105820000
F	-0.7185220000	0.5331730000	2.4031270000

Table S20. Cartesian coordinates of optimised F-ion adduct F–B(O(2-FC_6H_4))$_3$ [**1-F**] at M06-2X/def2-QZVPP (used in FIA calculations)

B	-0.5204550000	0.8983110000	0.8011000000
O	-0.0289870000	1.2495800000	-0.5456660000
C	1.2324540000	1.5351930000	-0.8312010000
C	1.9523460000	0.7005060000	-1.6928080000
C	3.2594910000	0.9476110000	-2.0495260000
C	3.9044680000	2.0711070000	-1.5486360000
C	3.2146270000	2.9274810000	-0.7055120000
C	1.8979620000	2.6666490000	-0.3543180000
H	1.3652150000	3.3380000000	0.3037840000
H	3.7027360000	3.8104350000	-0.3119220000
H	4.9330350000	2.2697300000	-1.8196500000
H	3.7686720000	0.2520700000	-2.7040550000
F	1.3465830000	-0.3934600000	-2.1761670000
O	-0.1648820000	-0.4859530000	1.1465520000
C	1.0581780000	-0.9849890000	1.1042570000
C	2.2032440000	-0.3414570000	1.5821960000
C	3.4520440000	-0.9400410000	1.5020970000
C	3.5984480000	-2.2058460000	0.9594350000
C	2.4729370000	-2.8752780000	0.4951880000
C	1.2395770000	-2.2666000000	0.5695540000
F	0.1661270000	-2.9240900000	0.1085970000
H	2.5467500000	-3.8645570000	0.0614750000

H	4.5721900000	-2.6731240000	0.8940710000
H	4.3174500000	-0.4007800000	1.8653740000
H	2.1060390000	0.6448890000	2.0119100000
O	-1.9666830000	0.9912690000	0.8081050000
C	-2.7983510000	0.2413910000	0.1109000000
C	-4.1586120000	0.3102360000	0.4444580000
C	-5.1317060000	-0.4041870000	-0.2172940000
C	-4.7730790000	-1.2446600000	-1.2639050000
C	-3.4366420000	-1.3385730000	-1.6147160000
C	-2.4619980000	-0.6128310000	-0.9442550000
H	-1.4317360000	-0.7028100000	-1.2523900000
H	-3.1338350000	-1.9893700000	-2.4253070000
H	-5.5291460000	-1.8125570000	-1.7898520000
H	-6.1634730000	-0.3017720000	0.0949470000
F	-4.5268370000	1.1124170000	1.4576450000
F	-0.0407220000	1.7990510000	1.7516150000

Table S21. Cartesian coordinates of optimised F-ion adduct F–B(O(3-FC_6H_4))$_3$ [**2-F**] at M06-2X/def2-QZVPP (used in FIA calculations)

B	-0.5170780000	-0.0039540000	1.8577080000
O	-1.4192610000	0.0940130000	0.7018990000
C	-2.0555730000	1.1733890000	0.2923330000
C	-2.6978340000	1.0935720000	-0.9520090000
C	-3.3838450000	2.1821610000	-1.4396110000
C	-3.4745040000	3.3794730000	-0.7563380000
C	-2.8356480000	3.4501870000	0.4746340000
C	-2.1365290000	2.3799650000	1.0061300000
H	-1.6604900000	2.4785880000	1.9694190000
H	-2.8858290000	4.3721260000	1.0407210000
H	-4.0196760000	4.2168700000	-1.1690300000
F	-3.9906280000	2.0746300000	-2.6380660000

H	-2.6447030000	0.1743020000	-1.5206580000
O	0.0121750000	-1.3688230000	1.8809540000
C	0.1874350000	-2.2527770000	0.9182970000
C	0.2440570000	-3.6035310000	1.2988220000
C	0.4702220000	-4.5970720000	0.3661580000
C	0.6463510000	-4.2976720000	-0.9787600000
C	0.5894350000	-2.9644290000	-1.3348980000
C	0.3685390000	-1.9421390000	-0.4367350000
H	0.3522670000	-0.9230050000	-0.7936950000
H	0.8212290000	-5.0642900000	-1.7207870000
H	0.5064150000	-5.6301660000	0.6894890000
H	0.1031070000	-3.8490570000	2.3431630000
O	0.5454100000	1.0074570000	1.8028550000
C	1.5076420000	0.9854000000	0.8882960000
C	2.6312030000	0.1650550000	1.0402960000
C	3.6342490000	0.1743030000	0.0884630000
C	3.5613350000	0.9924900000	-1.0317750000
C	2.4482070000	1.7992940000	-1.1598460000
C	1.4235930000	1.8121660000	-0.2361720000
H	0.5617050000	2.4526470000	-0.3750210000
F	2.3571980000	2.6048420000	-2.2345600000
H	4.3398910000	1.0026780000	-1.7820390000
H	4.4908860000	-0.4757780000	0.2132900000
H	2.6964720000	-0.4804770000	1.9050280000
F	-1.1857440000	0.2068300000	3.0525460000
F	0.7627990000	-2.6431150000	-2.6314730000

Table S22. Cartesian coordinates of optimised F-ion adduct F–B(O(4-FC_6H_4))$_3$ [**3-F**] at M06-2X/def2-QZVPP (used in FIA calculations)

B	-0.4300720000	-0.0220150000	1.8845760000
O	-1.3371330000	0.0392340000	0.7314520000

C	-1.9999600000	1.1024210000	0.3103520000
C	-2.5980070000	1.0276340000	-0.9548880000
C	-3.3149150000	2.0878860000	-1.4837070000
C	-3.4407390000	3.2482900000	-0.7471880000
C	-2.8674010000	3.3579240000	0.5020100000
C	-2.1519790000	2.2938240000	1.0332480000
H	-1.7158850000	2.3945280000	2.0155730000
H	-2.9778110000	4.2734890000	1.0691630000
F	-4.1360620000	4.2899690000	-1.2574340000
H	-3.7688220000	2.0110990000	-2.4635480000
H	-2.4866160000	0.1121360000	-1.5218430000
O	0.1751590000	-1.3538200000	1.8861000000
C	0.2334490000	-2.2482280000	0.9090940000
C	0.0909140000	-3.5971370000	1.2524190000
C	0.1984220000	-4.6057740000	0.3071330000
C	0.4467380000	-4.2685130000	-1.0064900000
C	0.5946360000	-2.9496190000	-1.3837400000
C	0.4902700000	-1.9447300000	-0.4346180000
H	0.6232540000	-0.9195060000	-0.7475400000
F	0.5506290000	-5.2438010000	-1.9374040000
H	0.0833380000	-5.6437660000	0.5923350000
H	-0.1105560000	-3.8457210000	2.2864090000
O	0.5818200000	1.0427930000	1.8384300000
C	1.5307740000	1.0573550000	0.9052550000
C	2.6950610000	0.2965090000	1.0470980000
C	3.6938460000	0.3306740000	0.0870850000
C	3.5315680000	1.1300900000	-1.0266110000
C	2.3964020000	1.8947960000	-1.1996850000
C	1.3995170000	1.8540400000	-0.2350480000
H	0.5014900000	2.4452730000	-0.3615150000

H	2.2852940000	2.5129970000	-2.0812580000
F	4.5036210000	1.1653460000	-1.9634100000
H	4.5882190000	-0.2682560000	0.2002810000
H	2.8048110000	-0.3326930000	1.9196580000
F	-1.1072190000	0.1515340000	3.0844530000
H	0.7984260000	-2.7001060000	-2.4171700000

Table S23. Cartesian coordinates of optimised F-ion adduct F–B(O(2,4-$F_2C_6H_3$))$_3$ [**4-F**] at M06-2X/def2-QZVPP (used in FIA calculations)

B	0.7416890000	-0.9624970000	-0.9772140000
O	-0.4436010000	-0.6551490000	-1.7638910000
C	-1.2982890000	0.3177290000	-1.4793000000
C	-0.9516860000	1.6252060000	-1.1363840000
C	-1.9171150000	2.5835310000	-0.8486430000
C	-3.2484110000	2.2403840000	-0.9134810000
C	-3.6449910000	0.9637810000	-1.2636850000
C	-2.6674510000	0.0313310000	-1.5378520000
F	-3.0470850000	-1.2090890000	-1.8585550000
H	-4.6904350000	0.6896950000	-1.3058430000
F	-4.1938310000	3.1618760000	-0.6380400000
H	-1.6243090000	3.5900260000	-0.5809240000
O	0.4381800000	-1.0655470000	0.4631240000
C	-0.7652950000	-1.3462910000	0.9481830000
C	-1.4587650000	-0.3984310000	1.7009220000
C	-2.7114410000	-0.6468930000	2.2413370000
C	-3.2926950000	-1.8764540000	2.0192100000
C	-2.6488620000	-2.8560160000	1.2909150000
C	-1.3977620000	-2.5800750000	0.7725700000
F	-0.7795470000	-3.5436580000	0.0887890000
H	-3.1066210000	-3.8210950000	1.1200330000
F	-4.5141770000	-2.1390180000	2.5240980000

H	-3.2316210000	0.1139780000	2.8068580000
O	1.7127920000	0.1382310000	-1.1282300000
C	2.8486590000	0.2379000000	-0.4677740000
C	3.5129800000	-0.7953840000	0.1989140000
C	4.7238470000	-0.5862040000	0.8477060000
C	5.2922170000	0.6674230000	0.8384760000
C	4.6760390000	1.7254610000	0.1979920000
C	3.4735600000	1.4911990000	-0.4340480000
F	2.8682910000	2.5197900000	-1.0476800000
H	5.1144050000	2.7144420000	0.1920630000
F	6.4702610000	0.8791680000	1.4611300000
H	5.2168190000	-1.4046480000	1.3551230000
H	-0.9938300000	0.5680790000	1.8413930000
H	0.0927230000	1.8964730000	-1.0954510000
H	3.0808620000	-1.7845650000	0.2047550000
F	1.2756800000	-2.1400730000	-1.4768860000

Table S24. Cartesian coordinates of optimised F-ion adduct F–B(O(3,5-$F_2C_6H_3$))$_3$ [**5-F**] at M06-2X/def2-QZVPP (used in FIA calculations)

B	-0.7099930000	0.0008170000	1.7494160000
O	-1.5532700000	0.1888140000	0.5550060000
C	-2.1811330000	1.2930220000	0.2102580000
C	-2.9849560000	1.2276080000	-0.9392590000
C	-3.6618500000	2.3483070000	-1.3567320000
C	-3.5953000000	3.5638790000	-0.7004080000
C	-2.7943130000	3.5950600000	0.4254500000
C	-2.0894690000	2.5110800000	0.9016450000
H	-1.4849230000	2.6161870000	1.7896170000
F	-2.7001170000	4.7577160000	1.0921900000
H	-4.1349080000	4.4338690000	-1.0451210000
F	-4.4295000000	2.2661670000	-2.4567550000

H	-3.0672980000	0.2961340000	-1.4825090000
O	-0.3019030000	-1.4029670000	1.7931140000
C	0.1243010000	-2.2328790000	0.8668640000
C	0.5198310000	-3.5052000000	1.3128690000
C	0.9933360000	-4.4261960000	0.4099200000
C	1.1053410000	-4.1731390000	-0.9444220000
C	0.7058200000	-2.9140580000	-1.3522830000
C	0.2209210000	-1.9444170000	-0.5030350000
H	-0.0706160000	-0.9867390000	-0.9048420000
F	0.7954080000	-2.6252060000	-2.6609740000
H	1.4828030000	-4.9091870000	-1.6390860000
F	1.3697070000	-5.6359940000	0.8610870000
H	0.4522670000	-3.7467670000	2.3647030000
O	0.4427930000	0.9101400000	1.7513990000
C	1.4263470000	0.8352450000	0.8649580000
C	2.5370350000	0.0235530000	1.1153900000
C	3.5545100000	-0.0174320000	0.1894030000
C	3.5375490000	0.7101250000	-0.9862750000
C	2.4292450000	1.5081940000	-1.1974610000
C	1.3773800000	1.5897920000	-0.3114990000
H	0.5298660000	2.2305550000	-0.5158980000
F	2.3837930000	2.2380010000	-2.3230720000
H	4.3470000000	0.6586510000	-1.7001800000
F	4.6202270000	-0.7963080000	0.4319260000
H	2.5845510000	-0.5685740000	2.0186240000
F	-1.4170810000	0.2608220000	2.9048870000

Table S25. Cartesian coordinates of optimised F-ion adduct F–B(O(2,3,4-$F_3C_6H_2$))$_3$ [**6-F**] at M06-2X/def2-QZVPP (used in FIA calculations)

B	0.0307370000	-0.0334490000	0.0521670000
O	-0.2872950000	1.2853640000	0.0858260000

C	0.6237560000	2.2870610000	0.1598350000
C	0.6976860000	3.0935110000	1.2809250000
C	1.5818020000	4.1612230000	1.3179580000
C	2.3895190000	4.4180730000	0.2305720000
C	2.3274990000	3.6163380000	-0.8976130000
C	1.4421010000	2.5551000000	-0.9277610000
F	1.3732620000	1.7882460000	-2.0097240000
F	3.1021250000	3.8625240000	-1.9449870000
F	3.2399700000	5.4409020000	0.2430880000
H	1.6432180000	4.7983340000	2.1889000000
H	0.0509810000	2.8887100000	2.1227740000
O	1.3193970000	-0.4364490000	0.2029370000
C	1.6903330000	-1.7374950000	0.0871950000
C	1.5923670000	-2.3772200000	-1.1401680000
C	1.9980990000	-3.6903290000	-1.2856020000
C	2.5154310000	-4.3670710000	-0.1931440000
C	2.6247920000	-3.7407250000	1.0300980000
C	2.2102220000	-2.4245160000	1.1688310000
H	2.2923200000	-1.9239300000	2.1234090000
H	3.0307740000	-4.2839040000	1.8717470000
F	2.9022740000	-5.6304940000	-0.3472930000
F	1.8895560000	-4.2894310000	-2.4635390000
F	1.0945770000	-1.7271770000	-2.1868600000
O	-0.9560410000	-0.9565320000	-0.0976370000
C	-2.2694890000	-0.6163540000	-0.1045690000
C	-2.8584120000	-0.1411310000	1.0581590000
C	-4.2017080000	0.1800130000	1.0890180000
C	-4.9650080000	0.0131390000	-0.0552150000
C	-4.3939300000	-0.4671570000	-1.2144980000
C	-3.0431290000	-0.7810900000	-1.2384860000

H	-2.5839950000	-1.1577870000	-2.1418040000
H	-5.0056850000	-0.5913670000	-2.0968950000
F	-6.2570090000	0.3265970000	-0.0130470000
F	-4.7466890000	0.6428580000	2.2060930000
F	-2.1205350000	0.0167820000	2.1542500000

Table S26. Cartesian coordinates of optimised F-ion adduct F–B(O(2,4,6-$F_3C_6H_2$))$_3$ [**7-F**] at M06-2X/def2-QZVPP (used in FIA calculations)

B	0.1120470000	0.2994950000	1.2851890000
O	-0.5697800000	0.5327420000	-0.0076970000
C	-1.7696740000	1.0691910000	-0.1116530000
C	-2.8018750000	0.3699340000	-0.7395460000
C	-4.0712350000	0.8821980000	-0.9379740000
C	-4.3302760000	2.1533830000	-0.4718820000
C	-3.3665400000	2.9025180000	0.1678010000
C	-2.1092820000	2.3486170000	0.3335360000
F	-1.1822740000	3.0841530000	0.9399600000
H	-3.5748500000	3.8988830000	0.5322900000
F	-5.5562460000	2.6782520000	-0.6476890000
H	-4.8310220000	0.2935920000	-1.4329230000
F	-2.5458720000	-0.8643360000	-1.1789130000
O	0.6914560000	-1.0516340000	1.2220270000
C	0.1593640000	-2.0012390000	0.4712980000
C	-0.7630740000	-2.9211300000	0.9644180000
C	-1.2965210000	-3.9489390000	0.2056050000
C	-0.8953950000	-4.0549300000	-1.1082190000
C	0.0143500000	-3.1819230000	-1.6671990000
C	0.5166980000	-2.1742040000	-0.8660710000
F	1.4034430000	-1.3317920000	-1.3933230000
H	0.3218150000	-3.2696280000	-2.6998880000
F	-1.4004380000	-5.0440970000	-1.8671720000

H	-2.0110350000	-4.6366580000	0.6360610000
F	-1.1487150000	-2.8154620000	2.2362900000
O	1.2094560000	1.2398390000	1.4998150000
C	2.2548710000	1.2174370000	0.6877980000
C	3.3994820000	0.4723190000	0.9765610000
C	4.5254270000	0.4560690000	0.1729880000
C	4.5082520000	1.2161640000	-0.9765980000
C	3.4184920000	1.9831620000	-1.3259290000
C	2.3164190000	1.9661070000	-0.4882000000
F	1.2755760000	2.7270790000	-0.8211470000
H	3.4125250000	2.5802130000	-2.2271980000
F	5.5912160000	1.2166560000	-1.7744330000
H	5.3852000000	-0.1408380000	0.4435810000
F	3.4258950000	-0.2430750000	2.0985080000
F	-0.7796200000	0.4379600000	2.3300450000

Table S27. Cartesian coordinates of optimised F-ion adduct F–B(O(3,4,5-$F_3C_6H_2$))$_3$ [**8-F**] at M06-2X/def2-QZVPP (used in FIA calculations)

B	-0.3947810000	-0.1068900000	1.3072100000
O	-1.5551680000	-0.9302210000	0.9722600000
C	-2.7240000000	-0.4738040000	0.5612660000
C	-3.1185210000	0.8696280000	0.6197580000
C	-4.3694540000	1.2280100000	0.1673420000
C	-5.2663950000	0.3081530000	-0.3430290000
C	-4.8690390000	-1.0150180000	-0.3896580000
C	-3.6268660000	-1.4142460000	0.0476700000
H	-3.3443490000	-2.4568130000	-0.0062050000
F	-5.7256140000	-1.9188350000	-0.8800470000
F	-6.4767250000	0.6844520000	-0.7750580000
F	-4.7468170000	2.5102970000	0.2209800000
H	-2.4726290000	1.6365080000	1.0195320000

O	-0.1063410000	0.7071420000	0.1179650000
C	0.8587700000	1.5997350000	0.0004060000
C	1.8458070000	1.8365990000	0.9653330000
C	2.8118400000	2.7897850000	0.7242450000
C	2.8451850000	3.5348250000	-0.4390490000
C	1.8632790000	3.2937690000	-1.3826230000
C	0.8838310000	2.3491720000	-1.1831740000
H	0.1289520000	2.1837560000	-1.9396740000
F	1.8787610000	4.0101020000	-2.5122570000
F	3.7921630000	4.4582760000	-0.6464110000
F	3.7567870000	3.0150330000	1.6437490000
H	1.8770730000	1.2895230000	1.8956570000
O	0.7089800000	-0.9950010000	1.6574200000
C	1.3696190000	-1.7923360000	0.8394910000
C	0.9751260000	-2.1029350000	-0.4683620000
C	1.7551180000	-2.9497860000	-1.2266230000
C	2.9213330000	-3.5152890000	-0.7465740000
C	3.2971320000	-3.2061440000	0.5476900000
C	2.5482730000	-2.3646130000	1.3365420000
H	2.8726790000	-2.1372090000	2.3426840000
F	4.4237610000	-3.7436650000	1.0300770000
F	3.6618760000	-4.3315720000	-1.5068680000
F	1.3811080000	-3.2476260000	-2.4759230000
H	0.0743930000	-1.6975810000	-0.9036860000
F	-0.6247730000	0.6935070000	2.4181620000

Table S28. Cartesian coordinates of optimised H-ion adduct H–B(C_6F_5)$_3$ at M06-2X/def2-QZVPP (used in HIA calculations)

B	-0.0227520000	0.0348130000	0.7444830000
C	-1.4934470000	0.5523210000	0.2676020000
C	-2.0989350000	1.6032820000	0.9413300000

C	-3.3665790000	2.0732530000	0.6486070000
C	-4.0894490000	1.4812220000	-0.3695640000
C	-3.5258170000	0.4403480000	-1.0781530000
C	-2.2504480000	0.0057260000	-0.7543960000
F	-1.7667170000	-0.9868880000	-1.5087440000
F	-4.2122220000	-0.1303060000	-2.0713890000
F	-5.3160280000	1.9146810000	-0.6665100000
F	-3.9026790000	3.0875070000	1.3326010000
F	-1.4471720000	2.2266800000	1.9269340000
C	0.2626650000	-1.5129760000	0.3179870000
C	1.0459900000	-1.9145540000	-0.7508080000
C	1.2917620000	-3.2412880000	-1.0612610000
C	0.7285480000	-4.2349730000	-0.2859490000
C	-0.0732460000	-3.8855380000	0.7828810000
C	-0.2884410000	-2.5464260000	1.0597070000
F	-1.0840150000	-2.2762530000	2.0983310000
F	-0.6282110000	-4.8432380000	1.5305490000
F	0.9510620000	-5.5194000000	-0.5702500000
F	2.0545940000	-3.5742620000	-2.1055030000
F	1.5959170000	-1.0090960000	-1.5666530000
C	1.1945520000	1.0245000000	0.3028180000
C	1.1323610000	2.0248460000	-0.6512810000
C	2.1988280000	2.8564910000	-0.9549090000
C	3.3994440000	2.6925040000	-0.2950170000
C	3.5143020000	1.7011780000	0.6606600000
C	2.4221530000	0.8993410000	0.9371500000
F	2.5971380000	-0.0462920000	1.8649710000
F	4.6753980000	1.5331250000	1.2989690000
F	4.4404700000	3.4774330000	-0.5789650000
F	2.0833230000	3.8077790000	-1.8849610000

F	0.0141900000	2.2283920000	-1.3563160000
H	-0.0369380000	0.0567570000	1.9549850000

Table S29. Cartesian coordinates of optimised H-ion adduct H–B(OPh)$_3$ at M06-2X/def2-QZVPP (used in HIA calculations)

B	-0.2007950000	0.2404840000	0.9497590000
O	-1.5209030000	0.6615400000	0.4543180000
C	-2.5769740000	-0.1241590000	0.3977590000
C	-3.7905830000	0.4479270000	-0.0163380000
C	-4.9481640000	-0.3041640000	-0.0932320000
C	-4.9444720000	-1.6527440000	0.2415130000
C	-3.7493240000	-2.2266460000	0.6507610000
C	-2.5786670000	-1.4882000000	0.7280770000
O	0.6137860000	1.4527190000	1.1300790000
C	0.9369390000	2.3382070000	0.2018860000
C	0.5939480000	2.2555520000	-1.1562800000
C	0.9919660000	3.2473390000	-2.0387140000
C	1.7333920000	4.3429860000	-1.6190950000
C	2.0772560000	4.4300020000	-0.2767740000
C	1.6879280000	3.4486620000	0.6168730000
O	0.3611820000	-0.6617130000	-0.0897920000
C	1.3885900000	-1.4634800000	0.1099710000
C	1.6157130000	-2.4823440000	-0.8283120000
C	2.6709100000	-3.3643420000	-0.6856320000
C	3.5363920000	-3.2690330000	0.3972400000
C	3.3210580000	-2.2628950000	1.3279480000
C	2.2710200000	-1.3673120000	1.1964120000
H	3.9876340000	-2.1642730000	2.1769310000
H	4.3619820000	-3.9600790000	0.5093780000
H	2.8167550000	-4.1398070000	-1.4287900000
H	0.9388750000	-2.5642560000	-1.6697700000

H	2.1403140000	-0.5817360000	1.9269140000
H	-1.6644620000	-1.9704120000	1.0422920000
H	0.0210540000	1.4181670000	-1.5245220000
H	0.7126060000	3.1558080000	-3.0819740000
H	2.0365050000	5.1092570000	-2.3210740000
H	2.6564920000	5.2732490000	0.0816850000
H	1.9581310000	3.5218900000	1.6631830000
H	-3.7195530000	-3.2778420000	0.9132970000
H	-5.8669440000	0.1707990000	-0.4177210000
H	-5.8505710000	-2.2419030000	0.1813940000
H	-3.7988000000	1.4994750000	-0.2754920000
H	-0.2572540000	-0.3222070000	2.0419350000

Table S30. Cartesian coordinates of optimised H-ion adduct H–B(OC_6F_5)$_3$ at M06-2X/def2-QZVPP (used in HIA calculations)

B	0.1382800000	0.3158940000	1.5565740000
O	-0.5218850000	0.5862570000	0.2414980000
C	-1.7364340000	1.0614230000	0.1202050000
C	-2.6588270000	0.3851670000	-0.6851980000
C	-3.9439750000	0.8491200000	-0.8850410000
C	-4.3617120000	2.0152640000	-0.2712590000
C	-3.4761490000	2.7059300000	0.5328180000
C	-2.1865040000	2.2407680000	0.7209550000
F	-1.3691940000	2.9553970000	1.4851430000
F	-3.8684480000	3.8361660000	1.1204940000
F	-5.6030330000	2.4693180000	-0.4556340000
F	-4.7895970000	0.1718410000	-1.6610230000
F	-2.2892250000	-0.7461830000	-1.2823540000
O	0.7704530000	-1.0251400000	1.3951140000
C	0.2611210000	-1.9184180000	0.5742380000
C	-0.8362450000	-2.7076130000	0.9150710000

C	-1.3503590000	-3.6579530000	0.0524600000
C	-0.7778900000	-3.8456050000	-1.1903650000
C	0.3110440000	-3.0773060000	-1.5582870000
C	0.8119780000	-2.1270470000	-0.6904800000
F	1.8511210000	-1.3918040000	-1.0758250000
F	0.8661570000	-3.2551460000	-2.7569270000
F	-1.2675870000	-4.7618460000	-2.0275920000
F	-2.3992460000	-4.3971280000	0.4145110000
F	-1.4161900000	-2.5407250000	2.1011180000
O	1.2321940000	1.2661680000	1.7989350000
C	2.2677150000	1.2733370000	0.9762820000
C	3.4113700000	0.5198750000	1.2460090000
C	4.5115450000	0.5398540000	0.4104080000
C	4.5029090000	1.3192340000	-0.7304670000
C	3.3885240000	2.0819910000	-1.0191670000
C	2.2906350000	2.0571450000	-0.1778580000
F	1.2494810000	2.8235060000	-0.4833620000
F	3.3794800000	2.8473070000	-2.1112980000
F	5.5660580000	1.3446270000	-1.5364580000
F	5.5892470000	-0.1904460000	0.7003300000
F	3.4669810000	-0.2244410000	2.3434680000
H	-0.6503910000	0.3798860000	2.4818750000

Table S31. Cartesian coordinates of optimised H-ion adduct H–B(O(2-FC_6H_4))$_3$ [**1**-**H**] at M06-2X/def2-QZVPP (used in HIA calculations)

B	0.2827700000	0.1529080000	0.7848710000
O	0.8570690000	0.3067550000	-0.5779070000
C	1.2397560000	1.4655950000	-1.0679430000
C	2.0169620000	1.4624310000	-2.2370500000
C	2.4783810000	2.6139510000	-2.8314620000
C	2.1769230000	3.8491770000	-2.2672740000

C	1.4080760000	3.8881240000	-1.1169660000
C	0.9430340000	2.7208030000	-0.5250620000
H	0.3269550000	2.7782000000	0.3608000000
H	1.1546630000	4.8398500000	-0.6668300000
H	2.5355350000	4.7594700000	-2.7290660000
H	3.0743920000	2.5386580000	-3.7323320000
F	2.3210770000	0.2789600000	-2.7932620000
O	0.2694880000	-1.2924530000	1.0599450000
C	1.3495560000	-1.9819550000	1.3527250000
C	2.6646150000	-1.5050610000	1.3149660000
C	3.7355620000	-2.3180670000	1.6622710000
C	3.5398240000	-3.6322340000	2.0502670000
C	2.2426770000	-4.1328780000	2.0889990000
C	1.1871150000	-3.3192950000	1.7484330000
F	-0.0577410000	-3.8201060000	1.7953030000
H	2.0439500000	-5.1552120000	2.3853830000
H	4.3755970000	-4.2657880000	2.3158840000
H	4.7374530000	-1.9094430000	1.6186450000
H	2.8481580000	-0.4873560000	1.0037740000
O	-1.1025670000	0.6390970000	0.8473330000
C	-2.0893200000	0.2906380000	0.0435340000
C	-3.3050220000	0.9764480000	0.1863610000
C	-4.4135340000	0.7111100000	-0.5846100000
C	-4.3503110000	-0.2769430000	-1.5599590000
C	-3.1648500000	-0.9725120000	-1.7275960000
C	-2.0518280000	-0.6999710000	-0.9437870000
H	-1.1455710000	-1.2654550000	-1.0976910000
H	-3.0938150000	-1.7471390000	-2.4808670000
H	-5.2153380000	-0.4932450000	-2.1727450000
H	-5.3191430000	1.2810280000	-0.4186130000

F	-3.3858120000	1.9379810000	1.1221390000
H	0.9286950000	0.7869160000	1.6154690000

Table S32. Cartesian coordinates of optimised H-ion adduct H–B(O(3-FC_6H_4))$_3$ [**2**-**H**] at M06-2X/def2-QZVPP (used in HIA calculations)

B	-0.6490190000	0.0459540000	1.7055470000
O	-1.3909780000	0.2489650000	0.4358430000
C	-2.1033360000	1.3188390000	0.1605620000
C	-2.9165170000	1.2750200000	-0.9832630000
C	-3.6837060000	2.3660670000	-1.3188520000
C	-3.7011660000	3.5311950000	-0.5750580000
C	-2.8914350000	3.5692590000	0.5520020000
C	-2.0992870000	2.4970800000	0.9262310000
H	-1.4722230000	2.5699720000	1.8021030000
H	-2.8737780000	4.4676090000	1.1568140000
H	-4.3163380000	4.3702690000	-0.8688380000
F	-4.4568670000	2.2938590000	-2.4209830000
H	-2.9342500000	0.3793820000	-1.5904130000
O	-0.2897080000	-1.3827680000	1.7850610000
C	0.1045450000	-2.2505980000	0.8767400000
C	0.3207350000	-3.5683990000	1.3199650000
C	0.7543520000	-4.5516420000	0.4530830000
C	0.9908170000	-4.2791230000	-0.8887080000
C	0.7714540000	-2.9815480000	-1.3079900000
C	0.3377540000	-1.9697750000	-0.4783030000
H	0.1941710000	-0.9805580000	-0.8856460000
H	1.3310580000	-5.0377730000	-1.5797360000
H	0.9128640000	-5.5560190000	0.8267600000
H	0.1405690000	-3.7944710000	2.3628930000
O	0.5496930000	0.9175220000	1.7698270000
C	1.5248310000	0.8613770000	0.8685970000

C	2.6222620000	0.0131450000	1.0553040000
C	3.6418030000	-0.0264650000	0.1221740000
C	3.6113870000	0.7704090000	-1.0151850000
C	2.5250070000	1.6072010000	-1.1772090000
C	1.4863280000	1.6702590000	-0.2720210000
H	0.6508880000	2.3386910000	-0.4378560000
F	2.4769810000	2.3944740000	-2.2689970000
H	4.4009470000	0.7415310000	-1.7533950000
H	4.4751210000	-0.7009630000	0.2729900000
H	2.6497100000	-0.6213990000	1.9306940000
H	-1.3325850000	0.3158690000	2.6820890000
F	0.9923920000	-2.6862990000	-2.6038010000

Table S33. Cartesian coordinates of optimised H -ion adduct H–B(O(4-FC_6H_4))$_3$ [**3-H**] at M06-2X/def2-QZVPP (used in HIA calculations)

B	-0.5403810000	0.0430890000	1.7518580000
O	-1.2898550000	0.1954730000	0.4834700000
C	-2.0364190000	1.2403090000	0.1861700000
C	-2.8216960000	1.1727380000	-0.9744580000
C	-3.6307630000	2.2253900000	-1.3657840000
C	-3.6690320000	3.3698630000	-0.5938130000
C	-2.9116790000	3.4740430000	0.5529360000
C	-2.0961060000	2.4201700000	0.9426460000
H	-1.4962860000	2.5191810000	1.8353080000
H	-2.9490490000	4.3793520000	1.1456610000
F	-4.4567170000	4.4028070000	-0.9720060000
H	-4.2297280000	2.1542940000	-2.2648670000
H	-2.7841920000	0.2678650000	-1.5675060000
O	-0.0908430000	-1.3594040000	1.8303800000
C	0.1538340000	-2.2503450000	0.8843070000
C	0.1345160000	-3.6002320000	1.2645370000

C	0.4145410000	-4.6192060000	0.3685050000
C	0.7163070000	-4.2982660000	-0.9383520000
C	0.7462510000	-2.9830640000	-1.3523940000
C	0.4680050000	-1.9644890000	-0.4530550000
H	0.5079930000	-0.9438670000	-0.8013600000
F	0.9888030000	-5.2859930000	-1.8225780000
H	0.3934880000	-5.6540070000	0.6864000000
H	-0.1073930000	-3.8392020000	2.2923530000
O	0.6064760000	0.9858890000	1.8123960000
C	1.5688990000	0.9683540000	0.8918130000
C	2.6962500000	0.1563890000	1.0478870000
C	3.7127490000	0.1507920000	0.1058760000
C	3.6044750000	0.9610150000	-1.0062300000
C	2.5064040000	1.7750630000	-1.1950050000
C	1.4922980000	1.7745070000	-0.2478720000
H	0.6255680000	2.4084790000	-0.3863100000
H	2.4379720000	2.4008890000	-2.0757010000
F	4.5942170000	0.9590840000	-1.9258580000
H	4.5769600000	-0.4889030000	0.2298630000
H	2.7612880000	-0.4833610000	1.9177210000
H	-1.2359430000	0.2845810000	2.7308230000
H	0.9932700000	-2.7431230000	-2.3787370000

Table S34. Cartesian coordinates of optimised H-ion adduct H–B(O(2,4-$F_2C_6H_3$))$_3$ [**4-H**] at M06-2X/def2-QZVPP (used in HIA calculations)

B	0.3484060000	-0.5745460000	-0.5857850000
O	-0.7925320000	-0.2161280000	-1.4456190000
C	-1.4790680000	0.9084590000	-1.3926920000
C	-1.1978330000	2.0277960000	-0.6013960000
C	-2.0024450000	3.1617440000	-0.6236510000
C	-3.1086730000	3.1945020000	-1.4404560000

C	-3.4363060000	2.1153750000	-2.2393010000
C	-2.6243240000	1.0020910000	-2.1985020000
F	-2.9498630000	-0.0443060000	-2.9680190000
H	-4.3061260000	2.1335000000	-2.8823080000
F	-3.8948800000	4.2907260000	-1.4706110000
H	-1.7560170000	4.0133640000	-0.0036220000
O	-0.0357070000	-0.5049430000	0.8572290000
C	-0.9401050000	-1.3533560000	1.3277890000
C	-2.3046340000	-1.0621590000	1.3342020000
C	-3.2470820000	-1.9330620000	1.8642880000
C	-2.8210650000	-3.1312640000	2.3940400000
C	-1.4838510000	-3.4748630000	2.4128330000
C	-0.5733240000	-2.5850790000	1.8778620000
F	0.7217960000	-2.9278000000	1.9084540000
H	-1.1506820000	-4.4159970000	2.8293690000
F	-3.7185060000	-3.9927490000	2.9115100000
H	-4.2987390000	-1.6804660000	1.8550950000
O	1.3959550000	0.4381490000	-0.7908760000
C	2.6441660000	0.3012550000	-0.3966960000
C	3.1276490000	-0.6761720000	0.4763840000
C	4.4709700000	-0.7421700000	0.8302290000
C	5.3521490000	0.1811700000	0.3178260000
C	4.9256180000	1.1727420000	-0.5464830000
C	3.5910910000	1.2123720000	-0.8876990000
F	3.1792020000	2.1694510000	-1.7289830000
H	5.6153610000	1.9003180000	-0.9530080000
F	6.6569810000	0.1327500000	0.6591860000
H	4.8166260000	-1.5095090000	1.5099920000
H	-2.6262940000	-0.1151820000	0.9214380000
H	-0.3287940000	2.0223180000	0.0374570000

H	2.4394440000	-1.3910110000	0.8997280000
H	0.7026180000	-1.7027020000	-0.9094940000

Table S35. Cartesian coordinates of optimised H-ion adduct H–B(O(3,5-$F_2C_6H_3$))$_3$ [**5-H**] at M06-2X/def2-QZVPP (used in HIA calculations)

B	-0.6479470000	0.0670470000	1.6956100000
O	-1.4000930000	0.2524610000	0.4281490000
C	-2.1216250000	1.3111120000	0.1465790000
C	-2.9226690000	1.2572430000	-1.0071020000
C	-3.6980820000	2.3407200000	-1.3412580000
C	-3.7409920000	3.5057750000	-0.5951180000
C	-2.9395950000	3.5278810000	0.5303180000
C	-2.1322260000	2.4821390000	0.9213980000
H	-1.5200490000	2.5743920000	1.8061350000
F	-2.9480970000	4.6411420000	1.2828850000
H	-4.3589110000	4.3458760000	-0.8768140000
F	-4.4614600000	2.2728550000	-2.4456970000
H	-2.9245380000	0.3637520000	-1.6163930000
O	-0.2752410000	-1.3569510000	1.7847860000
C	0.1194910000	-2.2281890000	0.8835580000
C	0.3639090000	-3.5317200000	1.3519210000
C	0.7950030000	-4.5010920000	0.4791910000
C	1.0069130000	-4.2704790000	-0.8672060000
C	0.7573330000	-2.9804880000	-1.2982940000
C	0.3232150000	-1.9613390000	-0.4803550000
H	0.1525580000	-0.9826530000	-0.9009450000
F	0.9500730000	-2.7116730000	-2.6006690000
H	1.3480920000	-5.0448460000	-1.5385660000
F	1.0236870000	-5.7398300000	0.9529810000
H	0.2119080000	-3.7589220000	2.3982170000
O	0.5454290000	0.9463650000	1.7382420000

C	1.5167830000	0.8815610000	0.8373960000
C	2.6238410000	0.0544830000	1.0570420000
C	3.6299430000	0.0222930000	0.1185580000
C	3.6063340000	0.7724210000	-1.0428660000
C	2.5022010000	1.5836460000	-1.2254550000
C	1.4615030000	1.6581640000	-0.3258060000
H	0.6186200000	2.3114380000	-0.5083520000
F	2.4502350000	2.3343380000	-2.3378590000
H	4.4067300000	0.7275380000	-1.7673360000
F	4.6909450000	-0.7723220000	0.3326960000
H	2.6754100000	-0.5573470000	1.9468570000
H	-1.3252280000	0.3418840000	2.6724860000

Table S36. Cartesian coordinates of optimised H-ion adduct H–B(O(2,3,4-$F_3C_6H_2$))$_3$ [**6-H**] at M06-2X/def2-QZVPP (used in HIA calculations)

B	-0.3684110000	0.4572420000	1.8478920000
O	-0.7849530000	1.3929700000	0.7572720000
C	-2.0395760000	1.6160800000	0.4433160000
C	-3.1524410000	0.9517410000	0.9695430000
C	-4.4422160000	1.2794190000	0.5735130000
C	-4.6562630000	2.2659900000	-0.3612380000
C	-3.5749090000	2.9332250000	-0.9108150000
C	-2.2946560000	2.6108290000	-0.5118230000
F	-1.2698220000	3.2721750000	-1.0587280000
F	-3.7665130000	3.8883820000	-1.8250890000
F	-5.8974850000	2.5932110000	-0.7569260000
H	-5.2891150000	0.7536060000	0.9933700000
H	-3.0064210000	0.1629190000	1.6914690000
O	-0.6552100000	-0.9483900000	1.4621590000
C	-0.1125680000	-1.6155860000	0.4584360000
C	0.1934660000	-2.9653220000	0.6739020000

C	0.7606690000	-3.7522730000	-0.3089240000
C	1.0496670000	-3.2088900000	-1.5475600000
C	0.7554840000	-1.8875550000	-1.7969510000
C	0.1721690000	-1.1041210000	-0.8118790000
H	-0.0464970000	-0.0703270000	-1.0291860000
H	0.9839170000	-1.4631440000	-2.7650100000
F	1.6069450000	-3.9860160000	-2.4891370000
F	1.0371280000	-5.0343550000	-0.0556670000
F	-0.0607450000	-3.5208690000	1.8584010000
O	1.0596280000	0.6931050000	2.0855150000
C	1.9871370000	0.5943240000	1.1420110000
C	2.8583280000	-0.4989170000	1.1544700000
C	3.8434420000	-0.6547620000	0.1989020000
C	3.9896990000	0.2958360000	-0.7950290000
C	3.1625440000	1.3969920000	-0.8230290000
C	2.1746490000	1.5466250000	0.1390890000
H	1.5142630000	2.4004930000	0.1048680000
H	3.2890900000	2.1375810000	-1.6011620000
F	4.9488410000	0.1309840000	-1.7184700000
F	4.6443320000	-1.7214960000	0.2329240000
F	2.7280680000	-1.4388370000	2.0879780000
H	-0.9782630000	0.6758080000	2.8805120000

Table S37. Cartesian coordinates of optimised H-ion adduct H–B(O(2,4,6-$F_3C_6H_2$))$_3$ [**7-H**] at M06-2X/def2-QZVPP (used in HIA calculations)

B	0.1639160000	0.2495570000	1.2574300000
O	-0.4898140000	0.5405800000	-0.0558450000
C	-1.6937560000	1.0550440000	-0.1633080000
C	-2.6626940000	0.4189790000	-0.9463920000
C	-3.9397220000	0.9089050000	-1.1470190000
C	-4.2803150000	2.0912840000	-0.5244440000

C	-3.3859470000	2.7744850000	0.2698260000
C	-2.1152270000	2.2485200000	0.4309030000
F	-1.2572110000	2.9309130000	1.1870850000
H	-3.6551040000	3.7030860000	0.7539760000
F	-5.5173790000	2.5915060000	-0.6986380000
H	-4.6442640000	0.3701760000	-1.7653050000
F	-2.3305930000	-0.7303960000	-1.5384970000
O	0.7871090000	-1.0912810000	1.0897510000
C	0.1519960000	-2.0415960000	0.4306310000
C	-0.8753580000	-2.8035020000	0.9857030000
C	-1.5282800000	-3.8202000000	0.3105570000
C	-1.1378190000	-4.0881850000	-0.9833730000
C	-0.1276660000	-3.3814690000	-1.6012020000
C	0.4851350000	-2.3704960000	-0.8845530000
F	1.4604870000	-1.6819470000	-1.4756610000
H	0.1685910000	-3.5921030000	-2.6194300000
F	-1.7563840000	-5.0727310000	-1.6608240000
H	-2.3209730000	-4.3782200000	0.7891980000
F	-1.2491650000	-2.5434070000	2.2407510000
O	1.2625260000	1.1853480000	1.5288440000
C	2.3053670000	1.2296350000	0.7131460000
C	3.4663270000	0.4931040000	0.9561600000
C	4.5911960000	0.5479000000	0.1526450000
C	4.5570600000	1.3755710000	-0.9491280000
C	3.4516480000	2.1407710000	-1.2502340000
C	2.3515020000	2.0511530000	-0.4141520000
F	1.2965280000	2.8139250000	-0.6975890000
H	3.4330690000	2.7927630000	-2.1124610000
F	5.6388000000	1.4459860000	-1.7466000000
H	5.4632650000	-0.0468460000	0.3863090000

F	3.5100220000	-0.2851260000	2.0357270000
H	-0.6386160000	0.3143930000	2.1761330000

Table S38. Cartesian coordinates of optimised H-ion adduct H–B(O(3,4,5-$F_3C_6H_2$))$_3$ [**8-H**] at M06-2X/def2-QZVPP (used in HIA calculations)

B	-0.2495490000	-0.0980100000	1.0092610000
O	-1.3869000000	-0.9377250000	0.6037880000
C	-2.6013140000	-0.4812780000	0.3925270000
C	-2.9549430000	0.8749620000	0.4330070000
C	-4.2649860000	1.2422090000	0.2103010000
C	-5.2572850000	0.3199210000	-0.0627090000
C	-4.8964440000	-1.0152860000	-0.1052220000
C	-3.6026730000	-1.4245110000	0.1159450000
H	-3.3535710000	-2.4762520000	0.0793030000
F	-5.8463120000	-1.9216030000	-0.3669300000
F	-6.5224320000	0.7030140000	-0.2818410000
F	-4.6022730000	2.5361990000	0.2513050000
H	-2.2234970000	1.6438180000	0.6328560000
O	0.1344930000	0.6810000000	-0.1972600000
C	0.9456710000	1.7166310000	-0.1649340000
C	1.7364200000	2.0602460000	0.9406240000
C	2.5462700000	3.1740170000	0.8765470000
C	2.6171320000	3.9739790000	-0.2477670000
C	1.8386960000	3.6211030000	-1.3361070000
C	1.0131550000	2.5217840000	-1.3116410000
H	0.4111690000	2.2773120000	-2.1761310000
F	1.8971990000	4.3866060000	-2.4322150000
F	3.4128350000	5.0508020000	-0.2859660000
F	3.2996650000	3.5027020000	1.9322570000
H	1.7371360000	1.4613160000	1.8395160000
O	0.8336280000	-0.9925460000	1.4430690000

C	1.4317740000	-1.9184730000	0.7179420000
C	1.1183450000	-2.2276990000	-0.6133140000
C	1.8168060000	-3.2246210000	-1.2594410000
C	2.8281710000	-3.9419910000	-0.6482480000
C	3.1325530000	-3.6257810000	0.6627810000
C	2.4587690000	-2.6395340000	1.3444750000
H	2.7209340000	-2.4182460000	2.3700060000
F	4.1109580000	-4.3068890000	1.2726450000
F	3.4880010000	-4.9083080000	-1.3007460000
F	1.5144540000	-3.5230320000	-2.5284380000
H	0.3411480000	-1.7073510000	-1.1517930000
H	-0.5128290000	0.6402020000	1.9527660000

Table S39. Cartesian coordinates of optimised $B(C_6F_5)_3$ at B3LYP/def2-TZVP (used in GEI calculations)

B	-0.0467070000	-0.1140300000	-0.1027530000
C	0.3801240000	1.3889230000	-0.2401780000
C	-0.0029730000	2.1782540000	-1.3284230000
C	0.3663360000	3.5060800000	-1.4655040000
C	1.1333650000	4.1033510000	-0.4732880000
C	1.5294200000	3.3637530000	0.6334710000
C	1.1622620000	2.0311040000	0.7241750000
F	1.5614590000	1.3667420000	1.8182900000
F	2.2536250000	3.9409450000	1.5920640000
F	1.4863990000	5.3784240000	-0.5824690000
F	-0.0061680000	4.2143000000	-2.5314320000
F	-0.7351240000	1.6474960000	-2.3182520000
C	-1.5068160000	-0.5524070000	-0.4678520000
C	-1.7835380000	-1.7586720000	-1.1197820000
C	-3.0665360000	-2.1635040000	-1.4487210000
C	-4.1427670000	-1.3560440000	-1.1036370000

C	-3.9212920000	-0.1526340000	-0.4467010000
C	-2.6226940000	0.2310640000	-0.1547520000
F	-2.4690060000	1.3966380000	0.4888970000
F	-4.9554960000	0.6159010000	-0.1059360000
F	-5.3799120000	-1.7331870000	-1.4012800000
F	-3.2791650000	-3.3136750000	-2.0875750000
F	-0.7817370000	-2.5698440000	-1.4866830000
C	0.9888120000	-1.1742150000	0.4109390000
C	2.3253250000	-1.1695600000	0.0004630000
C	3.2538680000	-2.0988340000	0.4399670000
C	2.8613650000	-3.0732570000	1.3483920000
C	1.5466010000	-3.1133330000	1.7944380000
C	0.6401870000	-2.1821700000	1.3150200000
F	-0.6125640000	-2.2585840000	1.7863170000
F	1.1739450000	-4.0427210000	2.6741080000
F	3.7407180000	-3.9643120000	1.7896020000
F	4.5131950000	-2.0678760000	0.0044230000
F	2.7534020000	-0.2585640000	-0.8849880000

Table S40. Cartesian coordinates of optimised $B(OPh)_3$ at B3LYP/def2-TZVP (used in GEI calculations)

B	0.0011310000	0.0014650000	0.0293830000
O	-1.2661620000	0.5098790000	0.0966060000
C	-2.4317930000	-0.1968170000	0.3017540000
C	-2.7972950000	-1.2572330000	-0.5203260000
C	-4.0130420000	-1.8972810000	-0.3078390000
C	-4.8626270000	-1.4815240000	0.7117050000
C	-4.4895950000	-0.4147920000	1.5226230000
C	-3.2759730000	0.2312270000	1.3200740000
O	1.0616920000	0.8357440000	-0.1907950000
C	1.0129380000	2.1962230000	-0.4075020000

C	0.2413750000	2.7466480000	-1.4252120000
C	0.2746780000	4.1198620000	-1.6397660000
C	1.0749350000	4.9397470000	-0.8514130000
C	1.8483490000	4.3767390000	0.1583030000
C	1.8215060000	3.0054980000	0.3825320000
O	0.2122820000	-1.3361790000	0.2178170000
C	1.4229330000	-1.9941120000	0.1720150000
C	2.2416710000	-1.9363020000	-0.9505140000
C	3.4243720000	-2.6667430000	-0.9705600000
C	3.7874890000	-3.4544210000	0.1165850000
C	2.9566270000	-3.5103100000	1.2306680000
C	1.7727720000	-2.7830580000	1.2618670000
H	3.2279010000	-4.1235940000	2.0809960000
H	4.7088610000	-4.0220840000	0.0943370000
H	4.0630270000	-2.6190620000	-1.8438520000
H	1.9574720000	-1.3215750000	-1.7939440000
H	1.1119260000	-2.8207810000	2.1180970000
H	-2.9737640000	1.0670620000	1.9375770000
H	-0.3814950000	2.1071580000	-2.0358990000
H	-0.3286680000	4.5482580000	-2.4304990000
H	1.0975860000	6.0080090000	-1.0245140000
H	2.4781340000	5.0054380000	0.7754510000
H	2.4221460000	2.5507330000	1.1595000000
H	-5.1453090000	-0.0803800000	2.3169580000
H	-4.2958850000	-2.7248550000	-0.9465260000
H	-5.8085730000	-1.9830070000	0.8709540000
H	-2.1340400000	-1.5796960000	-1.3115090000

Table S41. Cartesian coordinates of optimised $B(OC_6F_5)_3$ at B3LYP/def2-TZVP (used in GEI calculations)

B	0.0086670000	0.0041800000	0.0248510000
O	-1.2370520000	0.5547570000	0.1425900000
C	-2.3925490000	-0.1591280000	0.2757630000
C	-2.9174100000	-0.8924160000	-0.7844590000
C	-4.1295250000	-1.5564800000	-0.6609090000
C	-4.8377300000	-1.4851590000	0.5316430000
C	-4.3273940000	-0.7540100000	1.5962260000
C	-3.1117520000	-0.0964350000	1.4653810000
F	-2.6291390000	0.6007080000	2.4951140000
F	-5.0038800000	-0.6858150000	2.7420600000
F	-6.0037230000	-2.1166500000	0.6543520000
F	-4.6150810000	-2.2576430000	-1.6843610000
F	-2.2459220000	-0.9574810000	-1.9355120000
O	1.0972110000	0.8100030000	-0.1639540000
C	1.0413600000	2.1648650000	-0.3190110000
C	0.5163430000	2.7416840000	-1.4715990000
C	0.5256530000	4.1178260000	-1.6486400000
C	1.0734810000	4.9360350000	-0.6693500000
C	1.6065370000	4.3735480000	0.4829780000
C	1.5885120000	2.9958240000	0.6539830000
F	2.0992960000	2.4660080000	1.7656280000
F	2.1325880000	5.1566420000	1.4235740000
F	1.0869140000	6.2572570000	-0.8349690000
F	0.0134040000	4.6537980000	-2.7557670000
F	-0.0045400000	1.9593050000	-2.4199080000
O	0.1676130000	-1.3504950000	0.1143780000
C	1.3699120000	-1.9961040000	0.0988250000
C	1.7412680000	-2.7553220000	-1.0065140000

C	2.9231120000	-3.4840890000	-1.0015280000
C	3.7476320000	-3.4596200000	0.1154550000
C	3.3893960000	-2.7040310000	1.2243730000
C	2.2052250000	-1.9812650000	1.2116900000
F	1.8592760000	-1.2619830000	2.2816860000
F	4.1789610000	-2.6779370000	2.2970730000
F	4.8800490000	-4.1599020000	0.1230510000
F	3.2677300000	-4.2069780000	-2.0663390000
F	0.9564620000	-2.7847600000	-2.0837930000

Table S42. Cartesian coordinates of optimised $B(O(2\text{-}FC_6H_4))_3$ [**1**] at B3LYP/def2-TZVP (used in GEI calculations)

B	-0.5786640000	-0.6246180000	0.5440280000
O	0.4116200000	-1.1304640000	1.3479780000
C	1.7466610000	-1.2488850000	1.0925560000
C	2.2124700000	-1.7879330000	-0.1042870000
C	3.5595200000	-1.9823660000	-0.3417770000
C	4.4763270000	-1.6393050000	0.6460570000
C	4.0299140000	-1.1119070000	1.8530590000
C	2.6720110000	-0.9198900000	2.0763110000
H	2.3067310000	-0.5191890000	3.0128530000
H	4.7395180000	-0.8495350000	2.6268510000
H	5.5335510000	-1.7888620000	0.4713460000
H	3.8694220000	-2.4017710000	-1.2897890000
F	1.3091140000	-2.1309540000	-1.0477810000
O	-1.8141910000	-1.1762390000	0.7528180000
C	-2.9886740000	-0.6534400000	0.2826840000
C	-3.8095870000	-1.4127740000	-0.5408610000
C	-5.0350150000	-0.9105090000	-0.9639110000
C	-5.4506500000	0.3543270000	-0.5636550000
C	-4.6394670000	1.1214520000	0.2663490000

C	-3.4256330000	0.6075540000	0.6793430000
F	-2.6349750000	1.3396200000	1.4958440000
H	-4.9332600000	2.1080220000	0.5996870000
H	-6.4037390000	0.7470030000	-0.8926500000
H	-5.6642660000	-1.5111970000	-1.6075680000
H	-3.4704210000	-2.3960970000	-0.8394840000
O	-0.4463800000	0.3544570000	-0.4015570000
C	0.5534010000	1.2748940000	-0.5481900000
C	1.1411310000	1.4313960000	-1.8020950000
C	2.1076000000	2.3927560000	-2.0317680000
C	2.5001340000	3.2264180000	-0.9898720000
C	1.9169450000	3.0900850000	0.2642800000
C	0.9429570000	2.1225400000	0.4829750000
H	0.4665900000	2.0220210000	1.4497620000
H	2.2120990000	3.7419010000	1.0761010000
H	3.2558400000	3.9812520000	-1.1628950000
H	2.5374220000	2.4748670000	-3.0213730000
F	0.7551680000	0.6259210000	-2.8071810000

Table S43. Cartesian coordinates of optimised $B(O(3\text{-}FC_6H_4))_3$ [**2**] at B3LYP/def2-TZVP (used in GEI calculations)

B	-0.0079750000	0.0052490000	0.0041530000
O	-0.2030250000	1.3582860000	-0.0135930000
C	0.7608860000	2.3403390000	-0.0097800000
C	1.7716880000	2.3613550000	0.9455840000
C	2.6692710000	3.4143920000	0.9169120000
C	2.5973060000	4.4386140000	-0.0103500000
C	1.5715410000	4.3957540000	-0.9487220000
C	0.6514630000	3.3549460000	-0.9549580000
H	-0.1519880000	3.3181330000	-1.6778390000
H	1.4885710000	5.1853440000	-1.6843640000

H	3.3230850000	5.2395610000	0.0108380000
F	3.6544680000	3.4362220000	1.8399900000
H	1.8711630000	1.5825100000	1.6874030000
O	1.2613180000	-0.5020690000	-0.0025000000
C	1.6284060000	-1.8284740000	0.0216100000
C	2.5442090000	-2.2491870000	-0.9362950000
C	2.9752460000	-3.5627990000	-0.8944910000
C	2.5344140000	-4.4646230000	0.0580250000
C	1.6227530000	-4.0152400000	1.0069890000
C	1.1665460000	-2.7022500000	1.0006440000
H	0.4573020000	-2.3605060000	1.7410080000
H	1.2636420000	-4.6986420000	1.7656430000
H	2.9007620000	-5.4817200000	0.0512600000
F	3.8643070000	-3.9741140000	-1.8230650000
H	2.9130660000	-1.5671760000	-1.6893750000
O	-1.0822890000	-0.8399300000	-0.0092130000
C	-2.4139490000	-0.4941450000	0.0024950000
C	-2.9503290000	0.3342340000	0.9830470000
C	-4.3153800000	0.5963910000	0.9764630000
C	-5.1499910000	0.0412370000	0.0126490000
C	-4.5790370000	-0.7825620000	-0.9414850000
C	-3.2258510000	-1.0672760000	-0.9700870000
H	-2.8114080000	-1.7207000000	-1.7248260000
F	-5.3691290000	-1.3361630000	-1.8855740000
H	-6.2137090000	0.2335230000	-0.0043820000
H	-4.7358180000	1.2422080000	1.7365610000
H	-2.3076610000	0.7704400000	1.7345600000

Table S44. Cartesian coordinates of optimised $B(O(4\text{-}FC_6H_4))_3$ [**3**] at B3LYP/def2-TZVP (used in GEI calculations)

B	-0.0079750000	0.0052490000	0.0041530000
O	-0.2030250000	1.3582860000	-0.0135930000
C	0.7608860000	2.3403390000	-0.0097800000
C	1.7716880000	2.3613550000	0.9455840000
C	2.6692710000	3.4143920000	0.9169120000
C	2.5973060000	4.4386140000	-0.0103500000
C	1.5715410000	4.3957540000	-0.9487220000
C	0.6514630000	3.3549460000	-0.9549580000
H	-0.1519880000	3.3181330000	-1.6778390000
H	1.4885710000	5.1853440000	-1.6843640000
H	3.3230850000	5.2395610000	0.0108380000
F	3.6544680000	3.4362220000	1.8399900000
H	1.8711630000	1.5825100000	1.6874030000
O	1.2613180000	-0.5020690000	-0.0025000000
C	1.6284060000	-1.8284740000	0.0216100000
C	2.5442090000	-2.2491870000	-0.9362950000
C	2.9752460000	-3.5627990000	-0.8944910000
C	2.5344140000	-4.4646230000	0.0580250000
C	1.6227530000	-4.0152400000	1.0069890000
C	1.1665460000	-2.7022500000	1.0006440000
H	0.4573020000	-2.3605060000	1.7410080000
H	1.2636420000	-4.6986420000	1.7656430000
H	2.9007620000	-5.4817200000	0.0512600000
F	3.8643070000	-3.9741140000	-1.8230650000
H	2.9130660000	-1.5671760000	-1.6893750000
O	-1.0822890000	-0.8399300000	-0.0092130000
C	-2.4139490000	-0.4941450000	0.0024950000
C	-2.9503290000	0.3342340000	0.9830470000

C	-4.3153800000	0.5963910000	0.9764630000
C	-5.1499910000	0.0412370000	0.0126490000
C	-4.5790370000	-0.7825620000	-0.9414850000
C	-3.2258510000	-1.0672760000	-0.9700870000
H	-2.8114080000	-1.7207000000	-1.7248260000
F	-5.3691290000	-1.3361630000	-1.8855740000
H	-6.2137090000	0.2335230000	-0.0043820000
H	-4.7358180000	1.2422080000	1.7365610000
H	-2.3076610000	0.7704400000	1.7345600000

Table S45. Cartesian coordinates of optimised $B(O(2,4\text{-}F_2C_6H_3))_3$ [**4**] at B3LYP/def2-TZVP (used in GEI calculations)

B	0.6708060000	0.7054830000	-0.6002250000
O	-0.2790020000	1.2321630000	-1.4285310000
C	-1.6261390000	1.3407700000	-1.2324130000
C	-2.1759480000	1.9822980000	-0.1284140000
C	-3.5524010000	2.1338410000	-0.0015170000
C	-4.3678790000	1.6443140000	-1.0049830000
C	-3.8589120000	1.0139750000	-2.1278780000
C	-2.4862510000	0.8736350000	-2.2262820000
F	-1.9691180000	0.2733560000	-3.3068010000
H	-4.5074490000	0.6416250000	-2.9082530000
F	-5.7043920000	1.7867270000	-0.8964290000
H	-3.9874090000	2.6285510000	0.8554860000
O	0.4700650000	-0.0531010000	0.5264480000
C	-0.5641330000	-0.8747190000	0.8779600000
C	-1.0320700000	-0.8636870000	2.1863460000
C	-2.0289210000	-1.7412350000	2.5949960000
C	-2.5453830000	-2.6351820000	1.6738580000
C	-2.0980790000	-2.6856250000	0.3648670000
C	-1.1039350000	-1.8010680000	-0.0113380000

F	-0.6422580000	-1.8314820000	-1.2739810000
H	-2.5037580000	-3.3928430000	-0.3446400000
F	-3.5131320000	-3.4917680000	2.0572330000
H	-2.3996160000	-1.7381290000	3.6104230000
O	1.9521960000	1.0751300000	-0.9140790000
C	3.0848170000	0.5740160000	-0.3305290000
C	3.9878830000	1.4371000000	0.2767680000
C	5.1782700000	0.9629690000	0.8165780000
C	5.4500640000	-0.3906100000	0.7340660000
C	4.5805090000	-1.2825880000	0.1297310000
C	3.4058710000	-0.7799190000	-0.3997510000
F	2.5499190000	-1.6223120000	-1.0048060000
H	4.8076750000	-2.3373230000	0.0658540000
F	6.6005310000	-0.8657670000	1.2544010000
H	5.8860920000	1.6283300000	1.2907470000
H	-0.5974850000	-0.1594290000	2.8832010000
H	-1.5147130000	2.3716850000	0.6346930000
H	3.7461160000	2.4909710000	0.3150110000

Table S46. Cartesian coordinates of optimised $B(O(3,5\text{-}F_2C_6H_3))_3$ [**5**] at B3LYP/def2-TZVP (used in GEI calculations)

B	-0.0292660000	0.0040560000	-0.0012410000
O	-0.2164940000	1.3585010000	-0.0031670000
C	0.7628920000	2.3236130000	0.0033820000
C	1.7219270000	2.3688330000	1.0096700000
C	2.6392090000	3.4049060000	0.9809580000
C	2.6402090000	4.3905370000	0.0089800000
C	1.6596680000	4.3011120000	-0.9644910000
C	0.7144770000	3.2910690000	-0.9941250000
H	-0.0407200000	3.2581460000	-1.7658730000
F	1.6245290000	5.2415180000	-1.9265980000

H	3.3668210000	5.1895920000	0.0118540000
F	3.5744900000	3.4566740000	1.9477540000
H	1.7657640000	1.6240970000	1.7903330000
O	1.2391220000	-0.5041320000	-0.0344160000
C	1.6280120000	-1.8210050000	-0.0201380000
C	2.6260340000	-2.1906300000	-0.9160310000
C	3.0776430000	-3.4974970000	-0.8830270000
C	2.5850790000	-4.4456420000	-0.0022820000
C	1.5972940000	-4.0238010000	0.8707090000
C	1.1022110000	-2.7312740000	0.8914420000
H	0.3291410000	-2.4565980000	1.5927470000
F	1.0933280000	-4.9135570000	1.7464410000
H	2.9543760000	-5.4605290000	0.0052170000
F	4.0426540000	-3.8648500000	-1.7462470000
H	3.0395110000	-1.4763780000	-1.6130430000
O	-1.1070390000	-0.8364330000	-0.0041660000
C	-2.4375020000	-0.4921640000	0.0129070000
C	-2.9530430000	0.3700920000	0.9750210000
C	-4.3151140000	0.6165060000	0.9563990000
C	-5.1780370000	0.0440200000	0.0379900000
C	-4.6127290000	-0.8112170000	-0.8925960000
C	-3.2600780000	-1.0982920000	-0.9305470000
H	-2.8556900000	-1.7769280000	-1.6673490000
F	-5.4174550000	-1.3906090000	-1.8024580000
H	-6.2377800000	0.2519940000	0.0485360000
F	-4.8255570000	1.4532840000	1.8790280000
H	-2.3240180000	0.8441530000	1.7133680000

Table S47. Cartesian coordinates of optimised $B(O(2,3,4\text{-}F_3C_6H_2))_3$ [**6**] at B3LYP/def2-TZVP (used in GEI calculations)

B	0.0051550000	-0.0234100000	0.1368000000
O	-0.2711130000	1.3143100000	0.1905130000
C	0.6655340000	2.3151840000	0.2160230000
C	0.7695300000	3.1507170000	1.3187000000
C	1.6676950000	4.2118450000	1.3168010000
C	2.4582590000	4.4346600000	0.2052290000
C	2.3644000000	3.6102420000	-0.9087900000
C	1.4626460000	2.5553430000	-0.9000470000
F	1.3633750000	1.7718800000	-1.9794020000
F	3.1252970000	3.8261450000	-1.9834510000
F	3.3300020000	5.4536020000	0.1783700000
H	1.7595960000	4.8715210000	2.1684150000
H	0.1356160000	2.9633350000	2.1743610000
O	1.2961740000	-0.4634500000	0.2410350000
C	1.6864520000	-1.7704560000	0.0987370000
C	1.5466990000	-2.4144170000	-1.1278980000
C	1.9920650000	-3.7177380000	-1.2960810000
C	2.5895700000	-4.3761180000	-0.2290460000
C	2.7429400000	-3.7460540000	0.9914240000
C	2.2913420000	-2.4410090000	1.1518770000
H	2.4050270000	-1.9291050000	2.0974230000
H	3.2137660000	-4.2813220000	1.8042350000
F	3.0146920000	-5.6354100000	-0.4085330000
F	1.8458670000	-4.3232910000	-2.4762980000
F	0.9784530000	-1.7815160000	-2.1606860000
O	-1.0157880000	-0.9246860000	0.0152260000
C	-2.3439290000	-0.5872550000	-0.0470950000
C	-2.9998680000	-0.1325560000	1.0932190000

C	-4.3561850000	0.1577360000	1.0588590000
C	-5.0592920000	-0.0173690000	-0.1261310000
C	-4.4221400000	-0.4761160000	-1.2636560000
C	-3.0624480000	-0.7625800000	-1.2207710000
H	-2.5447980000	-1.1255370000	-2.0979360000
H	-4.9946460000	-0.6049420000	-2.1716950000
F	-6.3696500000	0.2676320000	-0.1426180000
F	-4.9700490000	0.5987100000	2.1590960000
F	-2.3263740000	0.0326420000	2.2387300000

Table S48. Cartesian coordinates of optimised $B(O(2,4,6\text{-}F_3C_6H_2))_3$ [**7**] at B3LYP/def2-TZVP (used in GEI calculations)

B	0.6651380000	0.5180890000	-0.6917690000
O	-0.3339110000	0.9370020000	-1.5297220000
C	-1.6329180000	1.1978100000	-1.2216200000
C	-1.9907630000	2.2328680000	-0.3594920000
C	-3.3066760000	2.5815120000	-0.1132590000
C	-4.2902360000	1.8630870000	-0.7703370000
C	-4.0025910000	0.8273940000	-1.6422970000
C	-2.6708190000	0.5144690000	-1.8520830000
F	-2.3570490000	-0.4854560000	-2.6863500000
H	-4.7850400000	0.2779650000	-2.1453020000
F	-5.5783960000	2.1840390000	-0.5523910000
H	-3.5490970000	3.3884310000	0.5628320000
F	-1.0044510000	2.9091100000	0.2490370000
O	0.5043940000	-0.1971180000	0.4693600000
C	-0.5698760000	-0.9564980000	0.8277390000
C	-1.3082250000	-0.6630180000	1.9719030000
C	-2.3513810000	-1.4617910000	2.4070570000
C	-2.6495680000	-2.5913550000	1.6647650000
C	-1.9473280000	-2.9443200000	0.5255950000

C	-0.9112170000	-2.1156780000	0.1339410000
F	-0.1947750000	-2.4259830000	-0.9568030000
H	-2.1909000000	-3.8323260000	-0.0392820000
F	-3.6622690000	-3.3789770000	2.0682660000
H	-2.9102610000	-1.2053150000	3.2952840000
F	-0.9926920000	0.4373900000	2.6662780000
O	1.9256430000	0.8541810000	-1.0951470000
C	3.0749180000	0.4551310000	-0.4773220000
C	3.5463780000	1.0777830000	0.6752640000
C	4.7514840000	0.7392280000	1.2656800000
C	5.5007650000	-0.2565330000	0.6640020000
C	5.0901610000	-0.9114070000	-0.4837370000
C	3.8765190000	-0.5373000000	-1.0349410000
F	3.4472360000	-1.1480420000	-2.1476970000
H	5.6897330000	-1.6860160000	-0.9392130000
F	6.6782240000	-0.6012410000	1.2176940000
H	5.0894000000	1.2397560000	2.1613390000
F	2.7961030000	2.0431890000	1.2244570000

Table S49. Cartesian coordinates of optimised B(O(3,4,5-$F_3C_6H_2$))$_3$ [**8**] at B3LYP/def2-TZVP (used in GEI calculations)

B	0.0000780000	0.0008080000	0.0366940000
O	-0.1991040000	1.3529550000	0.0220000000
C	0.7658330000	2.3334470000	0.0149780000
C	1.7430380000	2.3950860000	1.0017420000
C	2.6448690000	3.4444570000	0.9750350000
C	2.5900510000	4.4288720000	-0.0022110000
C	1.5996020000	4.3400770000	-0.9710970000
C	0.6825350000	3.3044970000	-0.9758390000
H	-0.0849240000	3.2624620000	-1.7353650000
F	1.5420940000	5.2871180000	-1.9152600000

F	3.4647570000	5.4377400000	-0.0083800000
F	3.5973540000	3.5255940000	1.9124480000
H	1.8183760000	1.6489680000	1.7790070000
O	1.2710550000	-0.5025090000	0.0306550000
C	1.6389320000	-1.8281870000	0.0180120000
C	2.5645790000	-2.2217310000	-0.9412480000
C	2.9995220000	-3.5347670000	-0.9476300000
C	2.5346710000	-4.4583910000	-0.0210750000
C	1.6155620000	-4.0323560000	0.9278900000
C	1.1606730000	-2.7258820000	0.9657660000
H	0.4440790000	-2.4345820000	1.7192650000
F	1.1666940000	-4.9182930000	1.8258500000
F	2.9622820000	-5.7232700000	-0.0402290000
F	3.8897610000	-3.9379920000	-1.8622140000
H	2.9460770000	-1.5201840000	-1.6692010000
O	-1.0718340000	-0.8473750000	0.0325330000
C	-2.4038250000	-0.5039110000	0.0246500000
C	-2.9402130000	0.3508750000	0.9808840000
C	-4.2999220000	0.6068110000	0.9506220000
C	-5.1305290000	0.0289300000	0.0003790000
C	-4.5644960000	-0.8258620000	-0.9358560000
C	-3.2093540000	-1.1028190000	-0.9366370000
H	-2.7936030000	-1.7775590000	-1.6711440000
F	-5.3609090000	-1.3886680000	-1.8526340000
F	-6.4406590000	0.2864510000	-0.0109060000
F	-4.8416220000	1.4294390000	1.8575670000
H	-2.3276110000	0.8209130000	1.7358840000

7. Crystallographic data

7.1 Single crystal X-ray diffraction

Single crystals of **1**, **7**, and **8** were grown in an N_2 filled glovebox by slow evaporation from dichloromethane at 5 °C. Crystallographic studies were undertaken on a single crystal mounted in Fomblin®Y and studied on an Agilent SuperNova Dual Atlas three-circle diffractometer using Mo- or Cu-Kα radiation and a CCD detector. Measurements were taken at 293(2) K with temperatures maintained using an Oxford cryostream. Data were collected, integrated and corrected for absorption within CrysAlisPro.[20] The absorption correction implemented a numerical absorption correction based on Gaussian integration over a multifaceted crystal model. The structures were solved by intrinsic phasing and refined against F^2 within SHELXL-2013.[21] The structures have been deposited with the Cambridge Structural Database [CCDC accession numbers: 2208652, 2208553, 2208552]. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7.2 Solid-state structures

Figure S62. Solid-state structure of compound **1**, top view, thermal ellipsoids drawn at 50% probability. H atoms and minor component of disorder omitted for clarity. C atoms in black, O in red, B in pink, F in green.

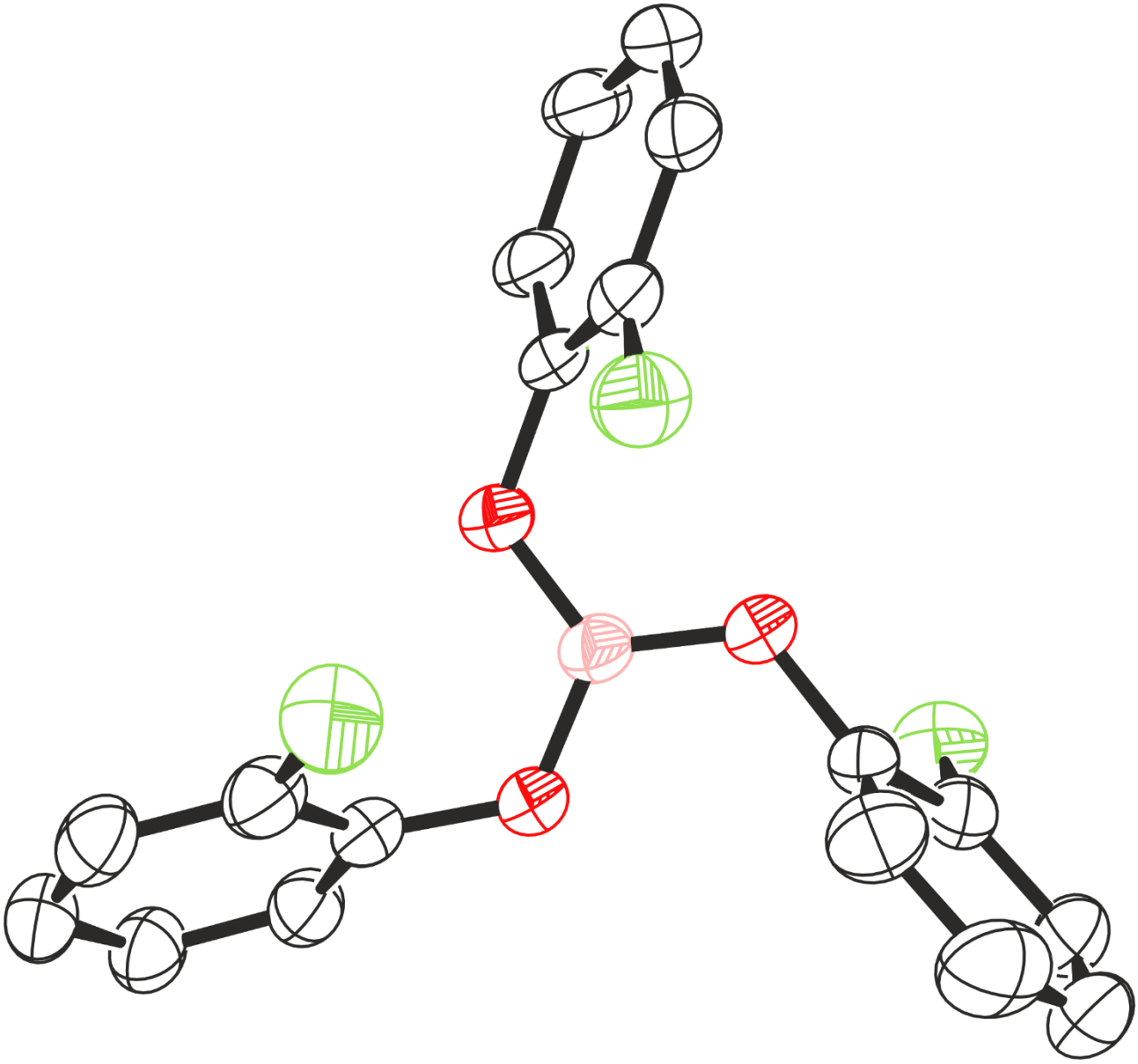


Figure S63. Solid-state structure of compound **1**, side view, thermal ellipsoids drawn at 50% probability. H atoms and minor component of disorder omitted for clarity. C atoms in black, O in red, B in pink, F in green.

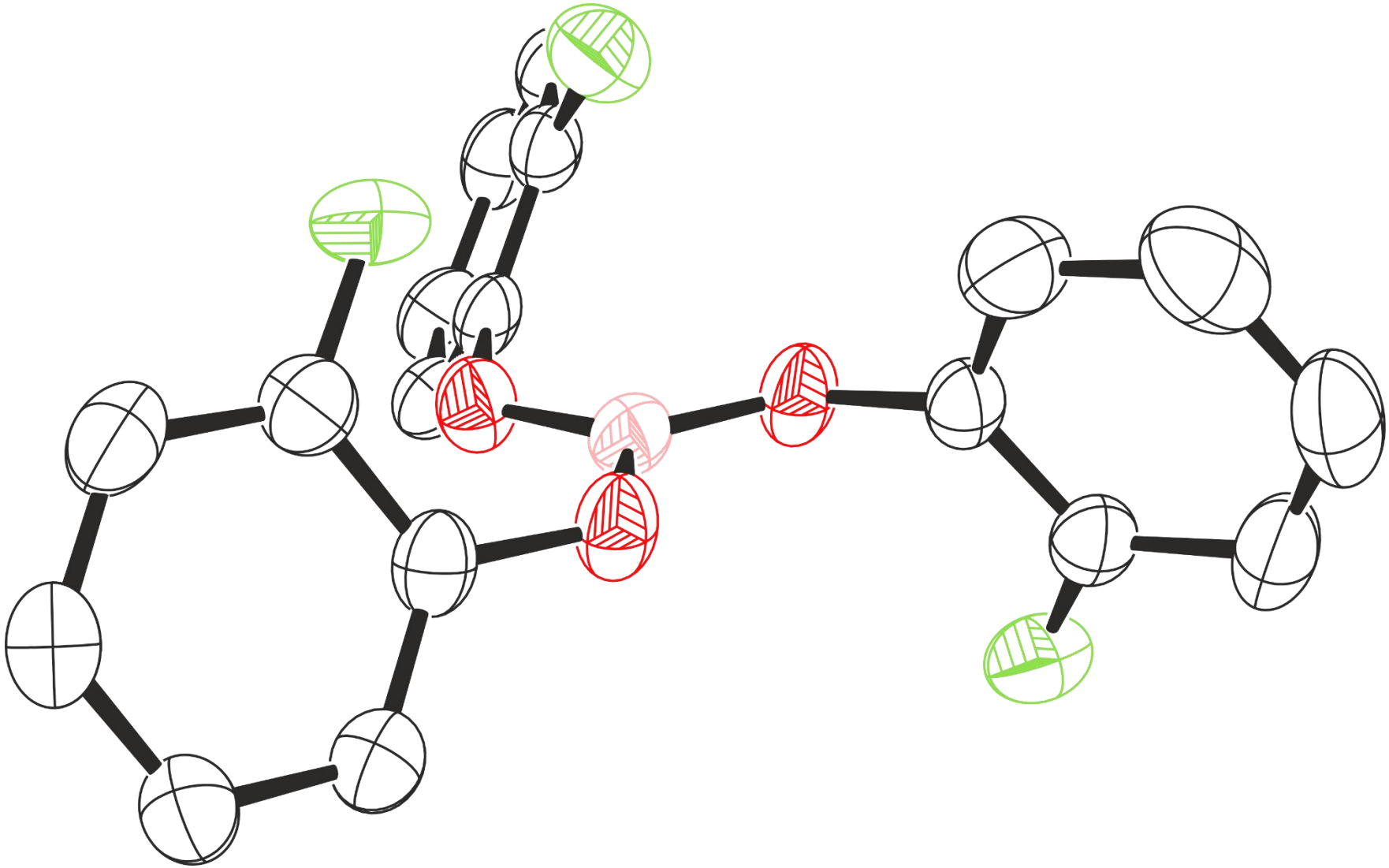


Figure S64. Solid-state structure of compound **7**, top view, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity. C atoms in black, O in red, B in pink, F in green.

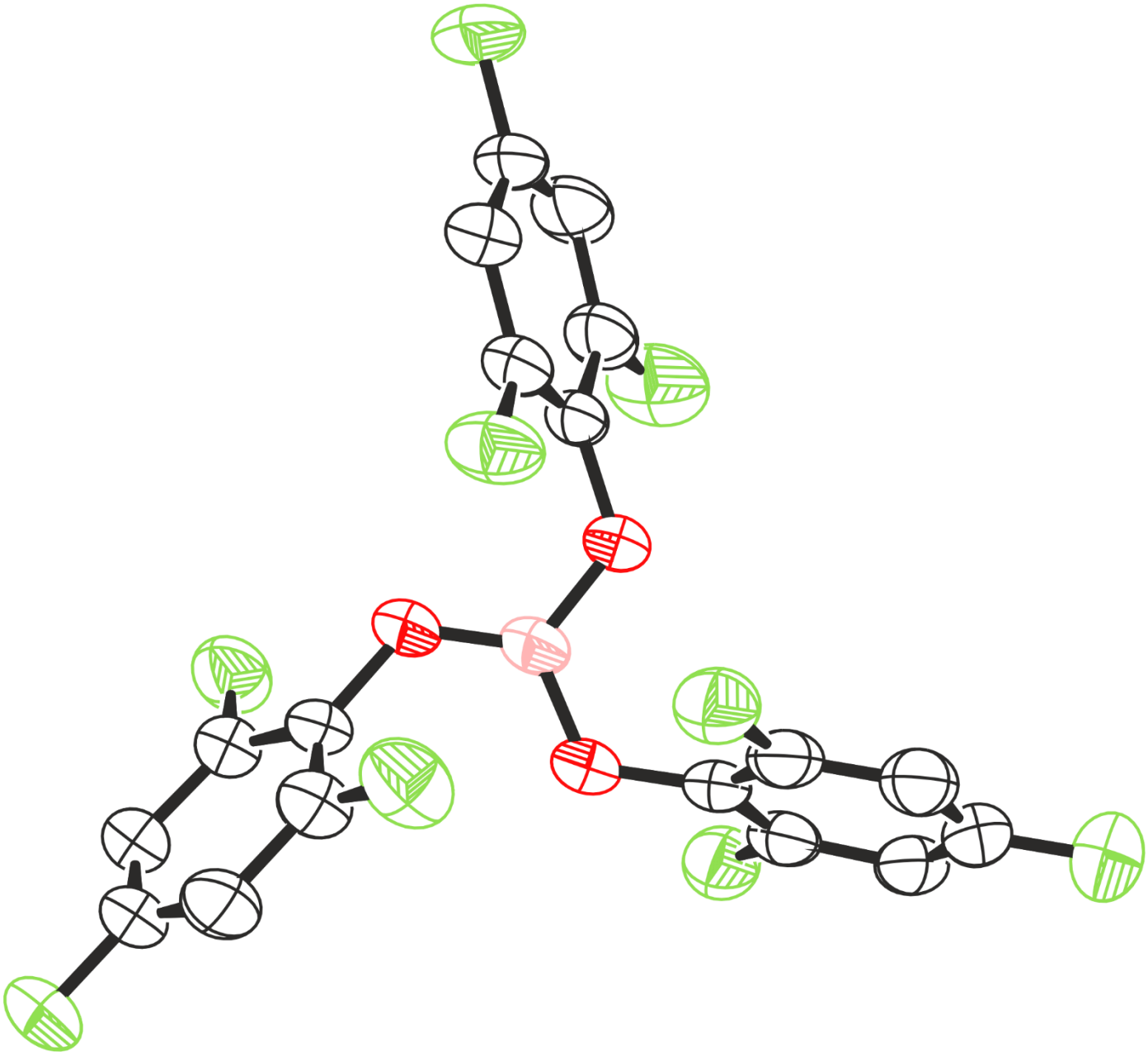


Figure S65. Solid-state structure of compound **7**, side view, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity. C atoms in black, O in red, B in pink, F in green.

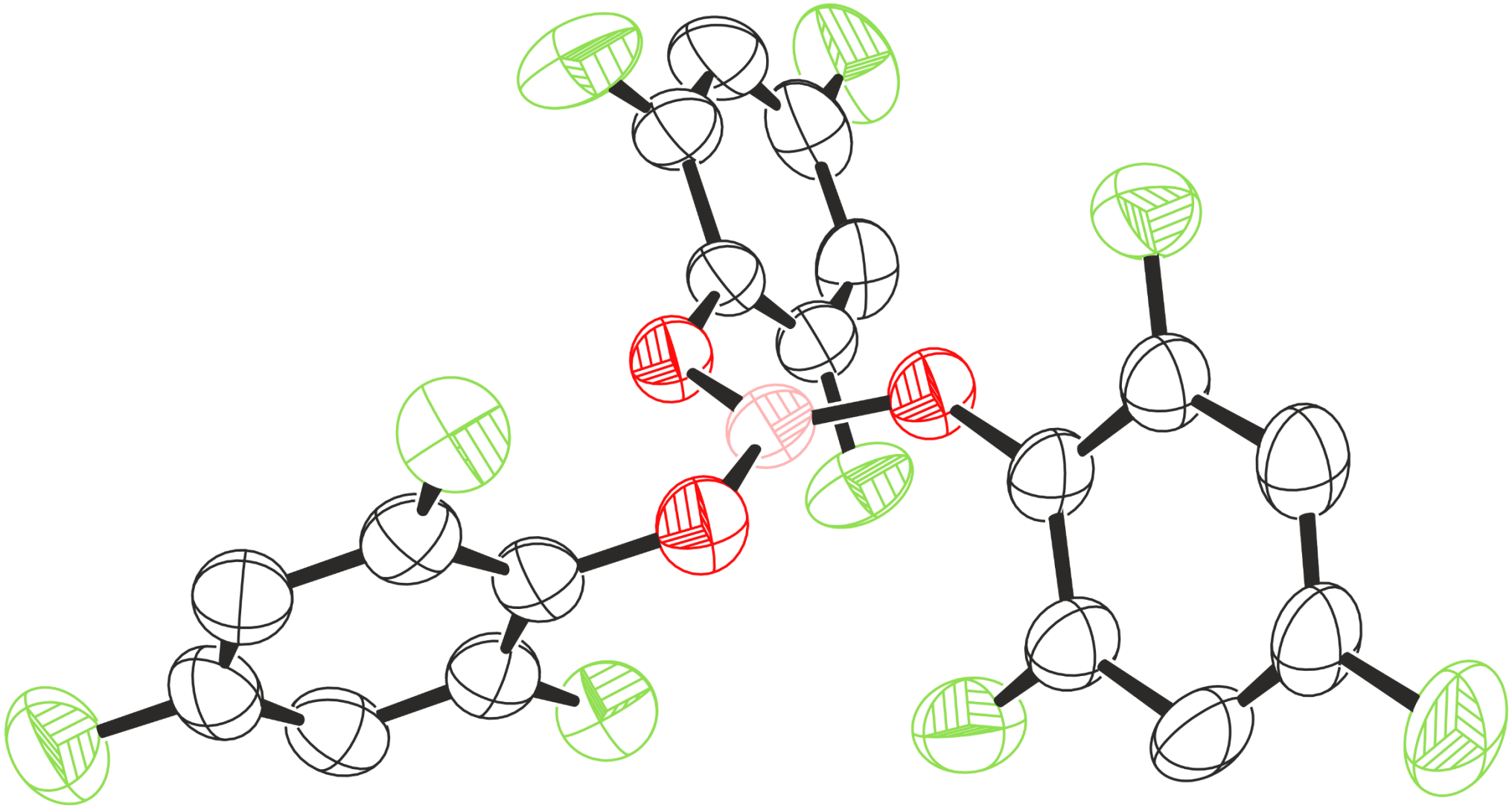


Figure S66. Solid-state structure of compound **8**, top view, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity. C atoms in black, O in red, B in pink, F in green.

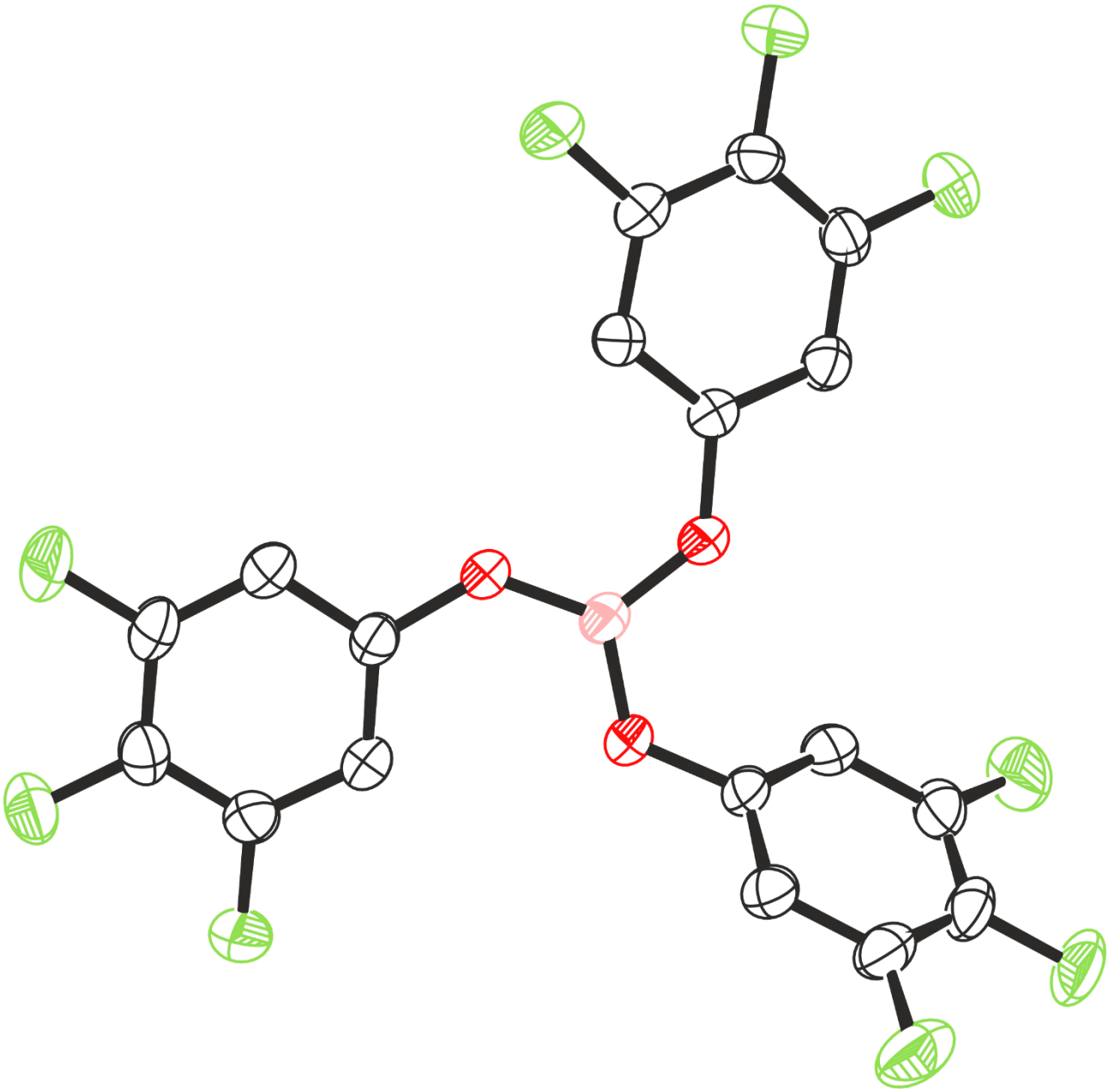
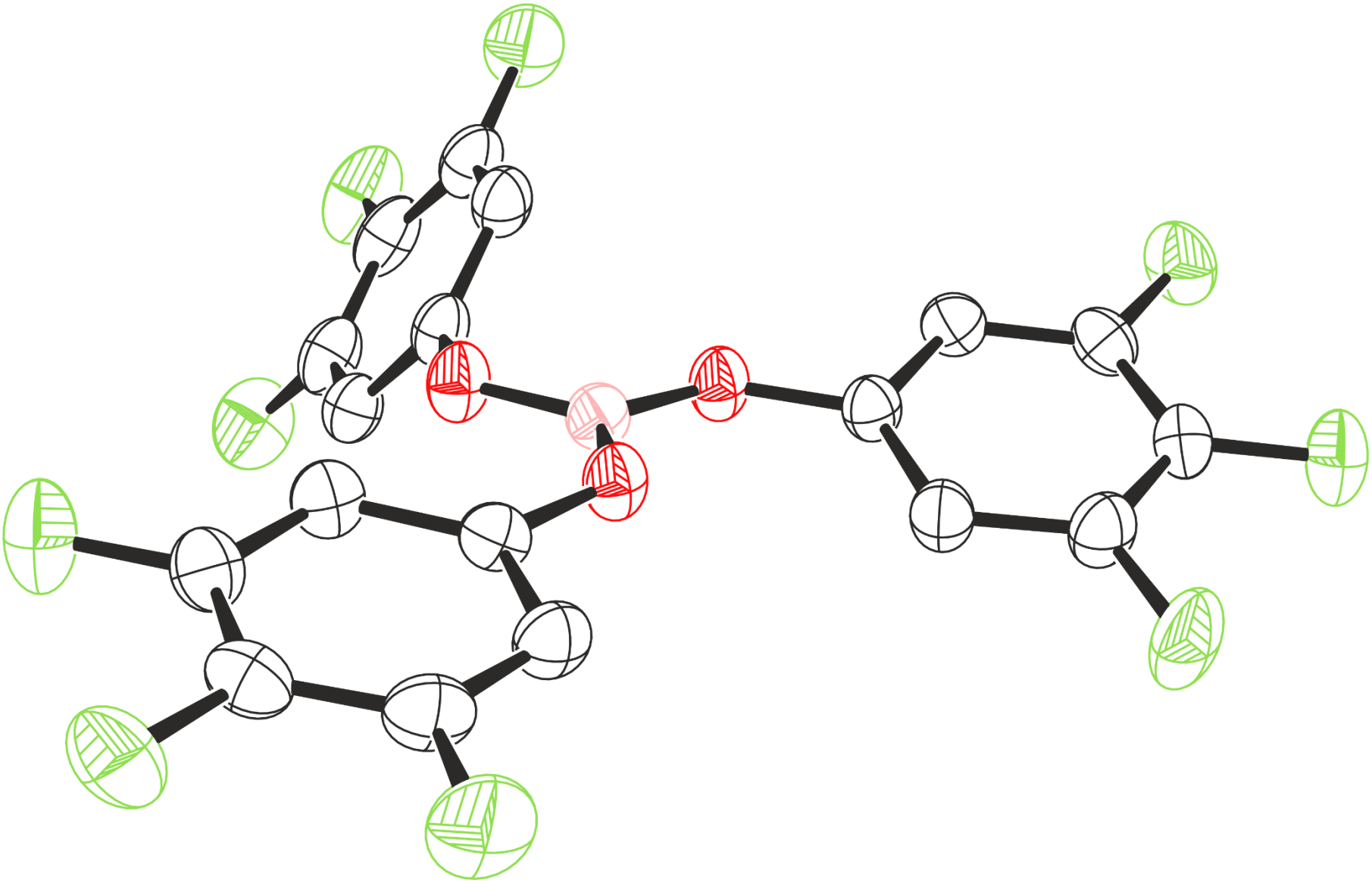


Figure S67. Solid-state structure of compound **8**, side view, thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity. C atoms in black, O in red, B in pink, F in green.



7.3 X-ray refinement data

Table S50: Crystal data and structure refinement for compound **1**.

Compound	**1**
Empirical formula	$C_{18}H_{12}BF_3O_3$
M_r	344.09
Crystal system	Triclinic
Space group	*P*-1
Temperature (K)	200
a, *b*, *c* (Å)	9.2006(9), 9.4849(9), 10.6212(7)
α, β, γ (°)	92.872(6), 101.180(7), 115.335(9)
Volume, V (Å^3)	812.53(14)
Z	2
Density, calc (g cm^{-3})	1.406
Absorption coefficient, μ (mm^{-1})	1.003
Crystal size (mm)	0.43 × 0.33 × 0.27
Radiation type	Cu K\a
Wavelength (Å)	1.54178
θ range (°)	4.29–72.94
Index ranges	-11 ≤ h ≤ 11
	-10 ≤ k 11
	-13 ≤ l ≤ 6
Reflections collected	5325
Independent reflections	2401
R(int)	0.0421
Absorption correction	Gaussian
Data / restraints / parameters	3126 / 0 / 247
Goodness of fit, S	1.041
Final R indices [I>2σ(I)]	R_1 = 0.0591
	wR_2 = 0.1611
R indices (all data)	R_1 = 0.0742
	wR_2 = 0.1845
Max residual electron density (*e*$^-$Å^{-3})	0.28
Min residual electron density (*e*$^-$Å^{-3})	-0.28

Table S51: Crystal data and structure refinement for compound **7**.

Compound	**7**
Empirical formula	$C_8H_6BF_9O_3$
M_r	452.04
Crystal system	Triclinic
Space group	*P*-1
Temperature (K)	200
a, *b*, *c* (Å)	11.3358(9), 13.4129(11), 13.6547(8)
α, β, γ (°)	69.358(6), 69.479(6), 72.094(7)
Volume, V (Å^3)	1779.1(3)
Z	4
Density, calc (g cm^{-3})	1.688
Absorption coefficient, μ (mm^{-1})	1.587
Crystal size (mm)	0.78 × 0.60 × 0.12
Radiation type	Cu K\a
Wavelength (Å)	1.54178
θ range (°)	4.19–72.18
Index ranges	-14 ≤ h ≤ 13
	-16 ≤ k 16
	-9 ≤ l ≤ 16
Reflections collected	13090
Independent reflections	6900
R(int)	0.0752
Absorption correction	Gaussian
Data / restraints / parameters	6900 / 0 / 559
Goodness of fit, S	1.052
Final R indices [I>2σ(I)]	R_1 = 0.0762
	wR_2 = 0.2203
R indices (all data)	R_1 = 0.1000
	wR_2 = 0.2634
Max residual electron density (*e*$^-$Å^{-3})	0.32
Min residual electron density (*e*$^-$Å^{-3})	-0.44

Table S52: Crystal data and structure refinement for compound **8**.

Compound	**8**
Empirical formula	$C_{18}H_6BF_9O_3$
M_r	452.02
Crystal system	Monoclinic
Space group	P 2_1/n
Temperature (K)	200
a, *b*, *c* (Å)	16.0890(3), 11.6330(3), 17.9172(4)
α, β, γ (°)	90, 94.5142), 90
Volume, V (Å^3)	3343.04(13)
Z	8
Density, calc (g cm^{-3})	1.796
Absorption coefficient, μ (mm^{-1})	1.689
Crystal size (mm)	0.52 × 0.30 × 0.13
Radiation type	Cu K\a
Wavelength (Å)	1.54178
θ range (°)	3.76–72.58
Index ranges	-18 ≤ h ≤ 19
	-14 ≤ k ≤ 8
	-21 ≤ l ≤ 21
Reflections collected	13847
Independent reflections	6470
R(int)	0.0207
Absorption correction	Gaussian
Data / restraints / parameters	6470 / 0 / 559
Goodness of fit, S	1.03
Final R indices [I>2σ(I)]	R_1 = 0.0356
	wR_2 = 0.0888
R indices (all data)	R_1 = 0.0474
	wR_2 = 0.0973
Max residual electron density (*e*$^-$Å^{-3})	0.22
Min residual electron density (*e*$^-$Å^{-3})	-0.22

Table S53. Comparison of structural parameters for compounds **7**, **8**, $B(OC_6F_5)_3$[2] and $B(OC_6H_5)_3$[22].

Compound	**$B(OC_6F_5)_3$[2]**		**3,4,5-$B(OC_6F_3H_2)_3$**		**2,4,6-$B(OC_6F_3H_2)_3$**		**$B(OC_6H_5)_3$[22]**	
B out of plane (Å)	Distance B atom to O1–O2–O3 plane (distortion from trigonal planar)							
Distance	0.26		0.012		0.019		0.014	
B–O torsion angle (^{0})	Angle between O1–O2–O3 plane and B–OX–CX plane							
B—O1	4.95		4.05		11.12		14.47	
B—O2	20.89		4.94		9.13		13.88	
B—O3	6.79		3.77		6.31		15.19	
B-O bond lengths (Å)								
B—O1	1.36(1)		1.373(2)		1.364(7)		1.362(3)	
B—O2	1.37(1)		1.365(2)		1.347(5)		1.360(3)	
B—O3	1.347(9)		1.361(2)		1.372(5)		1.359(2)	
O-C bond lengths (Å)								
O1—C	C1	1.387(8)	C10	1.373(2)	C10	1.383(4)	C1A	1.397(3)
O2—C	C7	1.372(7)	C20	1.386(2)	C20	1.387(5)	C7A	1.388(2)
O3—C	C13	1.350(8)	C30	1.381(2)	C30	1.369(5)	C13A	1.390(2)
Inclination Angle	Angle between O1–O2–O3 plane and C_6X_5 plane							
O1 ring	C1–C6	103.64	C10–C15	21.34	C10–C15	69.13	C1–C6	79.92
O2 ring	C7–C12	76.94	C20–C25	10.74	C20–C25	63.59	C7–C12	79.43
O3 ring	C13–C18	52.08	C30–C35	55.32	C30–C35	63.66	C13–C18	75.82

8. References

1 R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. Goodfellow, and P.Granger, *Solid State Nucl Magn Reson*., 2002, **4**, 458–483.

2 G. J. P. Britovsek, J. Ugolotti, and A. J. P. White, *Orgaometallics*, 2005, **24**, 1685–1691.

3 B. Chattopadhyay, J. E. Dannatt, I. L. Andujar-De Sanctis, K. A. Gore, R. E. Maleczka Jr, D. A. Singleton, and M. R. Smith III, *J. Am. Chem. Soc.,* 2017, **139**, 7864–7871.

4 M. A. Beckett, G. C. Strickland, J. R. Holland, and K. S. Varma, *Polym Commun.,* 1996, **37**, 4629–4631.

5 P. Erdmann, and L. Greb, *Angew. Chem. Int. Ed*., 2022, **61**, e2022114550.

6 O. M. Demchuk, W. Świerczyńska, K. Dziuba, S. Frynas, A. Flis, and K. M. Pietrusiewicz, Phosphorus, Sulfur., Silicon Telat. Elem., 2017, **192**, 64–68.

7 R. F. Childs, D. L. Mulholland, and A. Nixon, *Can. J. Chem.*, 1982, **60**, 809–812.

8 M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, and G. R. Hutchison, *J. Cheminform.*, 2012, **4**, 17.

9 F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73–78.

10 F. Weigend, and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

11 S. Grimme, J. G. Brandenburg, C. Bannwarth, and A. Hansen, *J. Chem. Phys.*, 2015, **143**, 54107.

12 P. Erdmann, and L. Greb, *ChemPhysChem*, 2021, **22**, 935–943.

13 A. R. Jupp, T. C. Johnstone, and D. W. Stephan, *Dalton. Trans.*, 2018, **47**, 7029–7035.

14 Y. Zhao, and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

15 F. Weigend, F. Furche, and R. Ahlrichs, *J. Chem. Phys.*, 2003, **119**, 12753–12762.

16 F. Neese, *J. Comput. Chem.*, 2003, **24**, 1740–1747; B. Helmich-Paris, B. de Souza, F. Neese, and R. Izsák, *J. Chem. Phys.*, 2021, **155**, 104109.

17 P. Erdmann, J. Leitner, J. Schwarz, and L. Greb, *ChemPhysChem*, 2020, **21**, 987–994.

18 P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.

19 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

20 SHELXL-2013, G.M. Sheldrick, University of Göttingen, Germany (2013).

21 CrysAlisPro, Agilent Technologies, Version 1.171.37.33 (release 27-03–2014 CrysAlis 171.NET)

22 I. M. Malkowsky, R. Fröhlich, U. Griesbach, H. Pütter, and S. R. Waldvogel, *Eur. J. Inorg. Chem.,* 2006, **8**, 1690–1697.